

STUDIES ON SOME ASPECTS OF ADSORPTION

(UNIO AND PILA SHELLS AS ADSORBENTS)

THESIS SUBMITTED FOR THE DEGREE OF

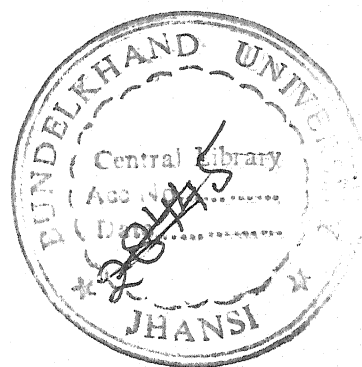
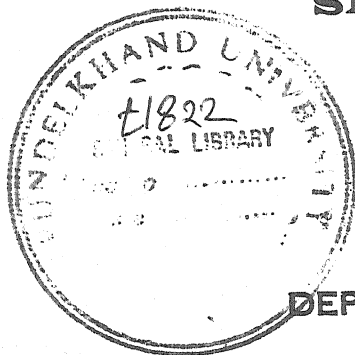
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C O N T E N T S

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C E R T I F I C A T E

This is to certify that the research work entitled
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Adsorbents)" which is being submitted as a thesis for Ph.D. in
Chemistry has been carried out by Shri SIYA RAM JATAV under my
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required by the ordinance of the Bundelkhand University and the
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I N T R O D U C T I O N

INTRODUCTION

A piece of solid or liquid matter is necessarily bounded by surfaces of contact with vacuum or atmosphere, or by interfaces on contact with another piece of solid or liquid matter. The mere existence of surface or interface can modify the properties of a material which interacts with the outside world. Thus many practical uses of materials depend on the state of their surface and their surface properties.

All solid substances are known to be capable of attracting molecules of gases or solutions to their surface with which they are in contact. This phenomenon is known as ADSORPTION. In other words ADSORPTION is a kind of adhesion which takes place at the surface of a solid or liquid in contact with another medium, resulting in an accumulation or increased concentration of molecules from that medium in the immediate vicinity of the surface. The solids that are used to adsorb gases or dissolved substances are called ADSORBENTS and the adsorbed molecules are usually referred to collectively as ADSORBATES. When a solid substance is dissolved in a liquid to form a solution, the solute usually tends to concentrate either on the

surface or in the bulk of the solvent. For example, soap solution (positive adsorption). On the other hand, inorganic salts such as ordinary table salt tends to concentrate in the bulk of aqueous solution rather than in its surface (negative adsorption).

The outsider materials penetrating the bulk of the substances leads to phenomenon of ABSORPTION. The distinction between ADSORPTION and ABSORPTION is not clear-cut, the non-committal word SORPTION is sometimes used. The process that will be considered in this study will be surface effects and the word adsorption will be used.

There are essentially three consecutive stages associated with the adsorption of materials from solutions by porous adsorbents (1):- the first step is the transport of the adsorbate to the exterior surface of the adsorbent;

the second step is the diffusion of the adsorbate into the pores of the adsorbent; and

the third step is the adsorption of solute on the interior surface of adsorbent.

At a fixed temperature, there is a definite relation between the number of molecules adsorbed on a surface and the pressure (if a gas) or the concentration (if a solution). The degree of adsorption depends upon five factors [2] :-

- i. The composition of the adsorbing material.
- ii. The condition of surface of the adsorbing material.
- iii. The material to be adsorbed.
- iv. The temperature.
- v. The pressure (if gas)

Traditional applications of physical adsorption include the use of Charcoal for removing poisonous gases from air; hydrocarbons from natural gas; oxygen, nitrogen or other gaseous impurities from helium during the separation and purification of the later. The adsorption of solute on the surface of solid in contact with solution is of fairly common occurrence. Adsorption from solution has been of more applications than that of gas phase. Its importance in dyeing, photography, brewing, the purification of water, the clarification of oil and in making lubricants more effective is well known. Soil and soil colloids with their large surface area (30 to 50 ac. per pound) are able by adsorption to remove from solution and

retain fertilizer components essential to plant growth [3]. Adsorption operations are used to remove impurities from liquids. Applications of adsorption from solutions on solid adsorbents have been considerably developed and become very important in many fields such as in purification process, water treatment process and analytical method [4]. For generations, it has been known that adsorption provides an effective method for removing organic solutes from dilute aqueous solutions.

In recent years, in order to reduce environmental pollution, there has been an escalating interest in multicomponent adsorption for cleaning industrial waste waters. Municipal and industrial waste water including organic compounds are sources of environmental pollution. Various adsorbents are useful in the removal of organic compounds and the regeneration of the water [5]. Many industries in India presently discharge untreated water on land or in natural streams causing pollution of surface water, ground water and land. As a result of rapid industrialisation, the water resources development schemes and water distribution systems are unable to keep pace with its increased demand. The reclamation of water for industrial reuse would minimise both these problems.

The emphasis is placed on the use of synthetic resins as adsorbents and on their performance relative to activated carbon for waste containing high concentrations of detergent or water containing a heterogeneous mixture of organic compounds such as domestic waste water or effluent from a secondary biological plant treating domestic sewage. The weak base resin seems to function best [6]. Activated carbons have usually been used as the adsorbents of waste water treatment [7-11]. Adsorption by activated carbon has also been emerged as most efficient and economical process for removing undesirable organic materials from aqueous solutions [12-14]. The removal of pollutants from aqueous effluents by adsorption on solid, produces high quality treated waste water. Many adsorbent materials have been tested [15-17].

Solid adsorbents, used industrially include active alumina, alumina impregnated with calcium chloride, activated bauxite, fuller's earth, silica gel, shell-base carbon, petroleum-base carbon and anhydrous calcium sulphate. Charcoals, carbon blacks, clays, earths, activated alumina or bauxite or other materials of highly adsorbent character are used to remove

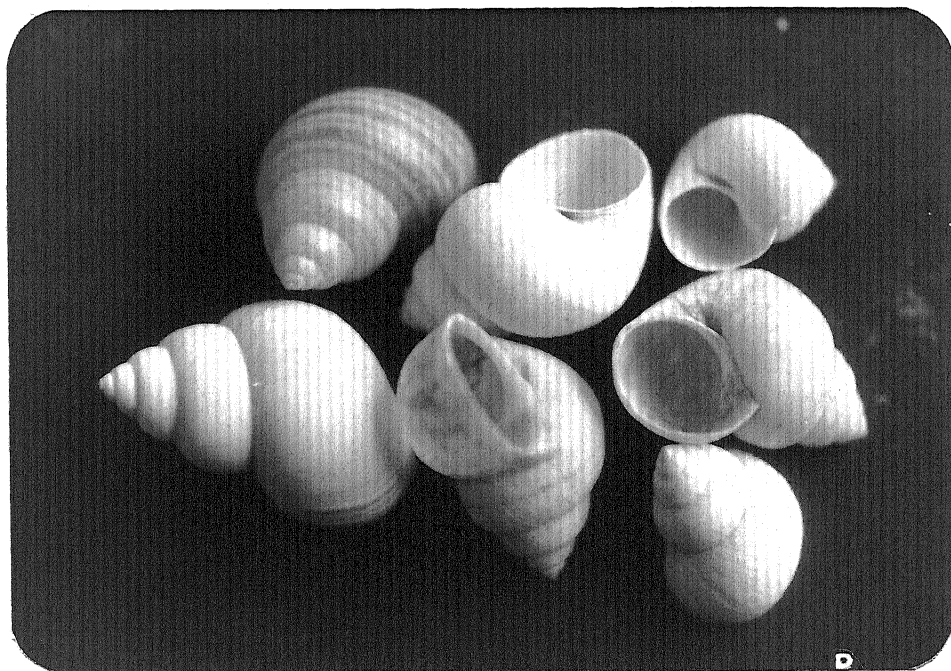
undesirable colours (and often odors) from sugar, vegetables, animal faeces and oils, among other substances. In a broad sense, decolorizing agents also embrace bleachings, which usually involve chemical reactions for removing colours. The adsorption behaviour of some anionic dyes used in textile industries, on newer synthesised adsorbents from guar gum has been studied and trimethyl aminised derivatives was found to be better adsorbents for the removal of colours of textile effluent in both alkaline and acidic conditions [18].

In view of high cost of adsorbents, there is a continuing search for low cost efficient adsorbents [18-22]. Adsorption capacity of five natural adsorbents namely chitin, chitosan and scales of three different species of fish: rohy, flounder and cod has been studied [23]. Chitosan has been put to many uses as adsorbent [24]. Chitosan derived from Prawn shell waste, shows specific adsorption capacity [25]. The particles of calcium carbonate may contribute surface area for anion adsorption [26].

The world is bestowed with vast natural resources. Two-third of its geographical area is covered by sea and ocean water and the remaining one-third land too, has a large number of rivers,

lakes, tanks and ponds. Innumerable aquatic animals of invertebrate phylum Mollusca (one of the largest and most important division of the animal kingdom) range in size from snails, little larger than a grain of sand to giant squids measuring more than 60 feet from the tip of the extended arms to the end of the tail. The phylum comprises six classes containing more than 1,00,000 living species and even greater number of fossil forms. All mollusks have a mantle and most have a shell in the adult stage. Although the mantle secretes the shell, it is not attached to it except at a single point or a few points, depending on the group of the animals. The shell is composed of mineral salts, mainly calcium carbonate with traces of calcium phosphate, magnesium carbonate, silica and organic matter [27,28].

Mollusks have always been of great interest and importance to man because of their use as food, tools, utensils, ornaments, money or religious emblems, by primitive man. They are an aid to anthropologists in tracing the trade routes of primitive people who fed on the animals and used the shells as money shells, are also of interest to collectors and are an important part of the tourists trade in some sea side areas. They are also important to oil



PILA SHELLS



UNIO SHELLS

geologist and paleontologist as index fossils and are one of the organisms most often used in carbon dating[29].

Unio & Pila are the prominent animals of phylum mollusca [30]. They are common aquatic animals, found in plenty, in and around the rivers, ponds, tanks, lakes, marshes & paddy fields. Their precious hard protective shells, left by them, are also found in abundance, in and around the water. Keeping in view the easy availability of desired amounts of the shells, it was thought worthwhile to employ the shells of Unio and Pila as adsorbents in the present study.

R E V I E W O F L I T E R A T U R E

REVIEW OF LITERATURE

The practical application of adsorbents is an old art [31,32]. One of the most common uses of adsorption is for purification of gases or liquids. Often the objective in such applications is to remove moisture, colour, odour, taste or in general, undesirable components of the mixture, without affecting appreciably the desirable components. In purification, the object is to collect and concentrate one or more components of the mixture, leaving behind the others. These two uses may be combined : one fraction of the mixture is left in the purified solution; the other is recovered as an adsorbate. Adsorbents are used not only for removing molecularly dispersed substances from solutions, but they are also used for removing colloiddally dispersed substances [33].

The invariable feature of adsorption at the solution-solid interface is the competition [34], which exists there between solvent and solute molecules for the surface. Adsorption studies have been made with a variety of organic solutes from aqueous and non-aqueous solutions, on solid adsorbents ranging from most hydrophilic oxides

to the most hydrophobic graphitized carbon blacks. Numerous examples are given [35]. There have been a large number of studies on the adsorption of surfactants at solid-water, oil-water and air-water interfaces [35-40]. Langmuir [41], Hildebrand [42], and many others have pointed out that the solubility of a substance in a given solvent may be expected to affect its adsorbability. The solubility of one substance in another depends upon the readiness with which the two molecular species can mix. Ideal behaviour in this respect is shown by relatively few substances. The components of such systems are usually quite similar in physical and chemical properties so that the intermolecular forces acting upon the molecules of one component are not greatly affected by the presence of the second.

Dubinin and Zaverina [43] have given an illustration of the influence of the solvent and solute. Not only the nature of the solute and solvent but the actual composition of a solution has strong influence on the extent and nature of the adsorption on an added solid [44]. It is well known that mixtures of solvents may be more effective than the individual solvent [45].

Several compilations of adsorbents are available [46,47]. The

list can not be considered complete because the number of adsorbents continually changes. Also, references to substances which may have special uses as adsorbents are often difficult to find. Since the nature of the substances to be adsorbed are not known, a standard substance has to be taken, such as "standard molasses solution" in sugar sirup decolorizing, against which the adsorbents can be tested. An alternative is to use a "standard reference adsorbent" against which other adsorbents can be tested via molasses solution. A great deal of work has been done to find some pure, easily analyzed substance which can be used as a substitute for the ill-defined colours and odours. Iodine in KI has been widely used, since the brown-coloured solutions can be decolorized and the extent of adsorption easily checked by titration with thiosulfate. Hassler [48] stated that the iodine adsorption test applied to charcoals seemed to be indicative more of the ability of the adsorbent to remove odors and flavours than to remove colour bodies. Permanganate solutions have also been used, as have methylene blue or ponceau red solutions. In testing the ability to remove odour and taste from water, phenol adsorption and adsorption of other pure substances have been

investigated [49,50]. A fundamental, weakness of these indirect tests is that there is no way of determining the correspondence between percent of colour reduction in, say, molasses solution and the removal of given percent of iodine from a stock solution. The tendency in applying adsorbents is more and more to test them on actual samples of the materials with which they are to be used, and to make the tests at a number of concentrations so as to avoid the errors of one point comparisons [51].

Attempts are sometimes made to list adsorbents in order of their efficiencies. However, the nature of adsorbate, its concentration, presence and absence of a solvent, temperature surface area and pore size of a particular sample of adsorbent, are all factors that can influence the efficiency of a given chemical species of adsorbent [44]. Alongwith the investigations of other adsorbents, researches have continued their intensive studies of such 'traditional' adsorbents on silica gels, alumina gels, ferro gels etc. as well as the corresponding oxides (quartz, Alumina and others differing in structure and origin [52].

The term carbon is widely used in industry to refer to activated charcoals which may contain considerable ash. The use of this term is apparently based on the observation when carbon is burned off a decolorizing carbon such as bone charcoal, which may contain 90 percent ash, the ash residue shows little or no decolorizing power. The charcoals and carbons run the gamut in composition from nearly pure carbon (purified graphites and sugar charcoals) to charcoals containing approximately 90 percent ash (bone cahrs) Ogawa [53] determined the elementary composition of a sugar charcoal. Mantell [54] has given an analysis of American bone char. A great deal has been written on the nature of the charcoal surface and the method of modifying it. The surface can be modified by suitable treatments so that it is organophilic or hydrophilic [55], Bartell and Lloyd [56] have prepared a charcoal, by activating purified sugar charcoal in a highly oxidizing atmosphere below 150°C, which approached the behaviour of hydrophilic silica in its adsorptive properties; it gave only negatively charged particles when suspended in water. High-temperature charcoal, activated near 1000°C, behaved as an organophilic adsorbent and on suspension in water showed both

positively and negatively charged particles.

Activated carbon is used for removing coloured impurities from solution, clay can remove coloured components from oil and bone char is used to remove impurities from sugar solutions in sugar refining [44]. Red colour of wines may be removed by filtering the wine through charcoal, the dark coloured impurities of crude sugar may be removed in the same way other decolorisers acting through purely chemical reactions are chlorine, sulfurous acid, permanganates and manganates all of which have been in sugar industry [57]. Activated charcoals, known for a long time as efficient absorbents of many gases vapours and dissolved substances in electrolytic solutions, have ion exchange properties determined mainly by the chemical nature of their surface [58-60]. Thus at the beginning of the twenties [61] it was found that pure charcoal activated at high temperature (900-1000°C) in air absorbs anions from electrolytic solutions and replaces them by an equivalent amount of hydroxyl ions i.e. it behaves as an anion exchange in the OH form.

Ordinary active charcoals, anion exchangers are however unstable and on contact with O_2 or air are transformed into their

stable modification i.e. oxidised charcoal, unlike ordinary charcoal, oxidised charcoal adsorbs cations and not anions from electrolytic solutions and hydrogen ions are liberated in the solutions. Thus oxidised charcoal behaves as a peculiar cationic in the H^+ form [62]. Modification of activated charcoal by oxidation in the air was first discovered in 1929 by Dubinin [63] and by Krupt and Dekadt [64]. It was later shown that carbon sorbents with cation exchange properties can also be obtained by processing activated charcoal by other oxidants in the gaseous [65,66] or liquid [67-70] phase. The production of activated carbon from byproducts and waste materials has increased [71]. Low temperature (500-600°C) chemical activation methods using $ZnCl_2$ and H_3PO_4 are being replaced in industry by High temperature (850-900°C) products, applying CO_2 or steams [72].

The gasification kinetics of carbonaceous materials have been investigated by several workers [73,74]. Carbon was also produced from walnut for adsorption study [75] and several fruits, stones and shells have similar composition and mechanical properties [76]. The carbon is also obtained by destructive distillation of wood or other carbonaceous material. It is activated by heating to

800-900°C, with steam or Carbondioxide, which results in a porous internal structure [77].

The bone black or bone char is the carboneous residue obtained as a result of distructive distillation of bones in the absence of air. The principal constituent of bone is tricalcium phosphate. Besides this compound, bones contain magnesium phosphate, calcium carbonate, some alkaline salts, fatty and cartilaginous matter intimately associated with the mineral contents [78]. Several investigations relating to adsorption of phenol from aqueous solutions by carbons and also to explore possibilities of using them in water treatment processes have been reported [79-84]. A good corelation between the surface activity of the activated carbon and the adsorption of phenols, amines and benzoic acid from aqueous solutions and ethyl alcohohal has been given by Oda et al [85,86].

Aluminas suitable for use as adsorbents are usually made by partial dehydration of hydroxides which may be prepared by hydrolysis of neutralization of the salts. Fibrous alumina [87,88] is prepared from the cleaned metal by amalgamating it, and reacting with water, water vapour or steam. Alumina, which is active as an adsorbent,

always contains some water. Moreover it should not be reactivated at very high temperature, because if all the water is driven off, structural change occurs (sintering) and alumina loses activity. Brockmann and Schodder [89] set up an arbitrary gradation of activities of alumina based on the chromatographic separation of certain dyestuffs; a highly active commercial alumina was deactivated to certain degrees by exposing it to moisture for a given time.

Alumina has enjoyed the position for sometime as the first choice for chromatography of new mixtures. It has probably been more used than any other adsorbent. It is a good adsorbent for most substances (with the proper solvent), has a large capacity, is white, insoluble, reasonably chemically inert (though the surface of the ordinary alumina gives a basic reaction), and readily obtainable. Alumina is, in fact, a very versatile adsorbent [90]. For chromatography, perhaps the commonest is activated alumina and it serves for both aqueous and non-aqueous solvents [91]. Some of the physical and other properties of alumina and related substances are discussed [51,92]. Adsorption behaviour of some amino acids on chemically prepared alumina has been discussed [93]. The interaction

of dyes with alumina has also been studied[94].

The clay minerals comprise a wide variety of substances some of which are, or many be converted into, adsorbents. The minerals are crystalline substances of colloidal dimensions which show exchange properties to varying degrees. The behaviours of clays are related to the size, shape and composition of the particles present, and to their exchange properties [95]. The size of the particles being within colloidal dimensions, the substances show relatively large surface areas. A mica from soil may have a surface area of some 60 square meters per gram, and a Kaolinite 80 square meters per gram [96]. Some natural clays will have particles larger than others, and the size can always be changed by physical and chemical treatment in activation and other processes. The shapes of the crystalline particles can be shown by electron microphotographs [97]. Montmorillonite, Kaolinites and some bentonites are composed of platelets. Attapulgitite is made up of fibrous particles. In composition, these substances are silicates. The Kaolinites are aluminosilicates. The bentonites are also aluminosilicates, but more complex. They are of different types: some have sodium, others

calcium as the chief exchangeable cation, but potassium and magnesium are also present. The behaviour of these substances towards water, electrolytes, and organic liquids depends very much on their composition [95].

Fuller's earth and other clays are used in extremely large quantities for bleaching, decolorizing, catalysis and a myriad of other applications. In using these substances in the laboratory for analytical work, it may be necessary to wash off traces of oily material which may be present [98]. Fuller's earth has been reported to have high natural adsorptive power [99]. Solution phase studies on the adsorption of dimethoate (O,O-dimethyl-S-(N-Methyl) carbamoylmethyl) phosphorodithioate on three sodium saturated clay minerals, i.e. bentonite, fuller's earth and Kaolinite & two soils i.e. Kapurthala soil and Keylong soil at 15 and 25°C have indicated that dimethoate is adsorbed by all the clay minerals and soils [100]. Diatomaceous earth also finds numerous adsorbent applications in food and chemical processing, not only in decolorizing, but as a filter aid and clarifying agent as well. Ever since their introduction by Strain [101] in this application the diatomaceous filter aids have seen increasing use in chromatography. In purifying the products of

organic chemical synthesis, e.g. decolorizing, carbons and clays often are used as contact adsorbents. They are stirred directly into a liquid-phase mixture or solution and subsequently removed by filtration. In some cases, as in contact filtration, the adsorbents are incorporated in the filtering medium. Contact filtration is widely used for removing coloured and carbon-forming material from lubricating oils. In other configuration, a liquid may be allowed to percolate by gravity or under pressure through a bed of solid adsorbents [102].

Silica, or silicic acid, reagent grade, is finding a great many applications in chromatography. The substance is inert and a good adsorbent for polar substances. It was found in Zechmeister's laboratory [103] that the strength of the adsorbent could be influenced by prewashing. The acetone-ether prewash yields an adsorbent of the same activity as is produced by heating the silicic acid at 200°C for about 40 minutes. Le Rosen [104] found that Merck reagent silicic acid was very responsive to this activation by prewashing technique. A number of investigations have been studied on the adsorption of alcohols from hydrocarbons to silica or glass [105]

Ram [106] has studied the time-rate adsorption of dyes on silica. Scolecite (Zeolite) a crystalline hydrated aluminium-silicate of alkali metal with three-dimensional anion network, has been used as adsorbent for separation of phospholipids by their layer chromatography [107]. Zeolites [108] are hydrated alumina-silicates of the alkali and alkaline earth metals, having Ca in their framework. The separation of phospholipids using silica gel has been reported earlier [109-111]. The use of scolecite for separation of organic acids, amino acids, carbohydrates [112], textile dyes [113] and food dyes [114] has been reported.

Phenol and phenolic compounds exist in the waste water from oil refineries, cake plants, phenolic resin plants and so on. Phenol is a weak acid and can be removed effectively from aqueous solution by anion exchange resins [115-117]. Adsorption equilibrium of phenol on anion exchange resins in the hydroxide form or the free base form is compared with that in the chloride form. For strong base anion exchange resins, there is a great difference of phenol adsorbed between hydroxide and chloride forms. Phenol adsorbed on resins in the hydroxide form can be desorbed by using hydrochloric acid [118].

Adsorption of metal ions in solution on vermiculite, bentonite, sericite and zeolite have been studied by batch method [119].

Adsorption on metal oxides from binary solutions (e.g. solution of benzene and methanol) have been investigated by several workers [122-125]. A number of organic substances have found use as adsorbents, particularly in applications where mildness of action is desired. Filter paper pulp makes an effective filter aid for charcoal adsorption columns [126]. Starch [127] and some other organic substances are also used as adsorbents [128].

Methanol adsorbs molecularly on the surfaces of Cu-Pd alloys at low temperatures and transforms to CH_3O or CO on warming, depending upon the alloy composition. On oxygen presorbed Cu-Pd alloy surface adsorption of methanol gives rise to H_2O and H_2CO [129]. The adsorption of methanol, formaldehyde and formic acid on Cu/ZnO and Cu/ZnO/ Cr_2O_3 have been studied [130] by transmission infrared spectroscopy. Methanol adsorbed dissociatively to form a methoxy and hydroxyl species. Formaldehyde adsorbed at 100°C on zinc site through the oxygen. Adsorbed formaldehyde was very unstable at 200°C forming methoxy and formate species. Formic acid adsorbed dissociatively to

produce bidentate formate and hydroxyl species.

The interactions between a mineral and electrolytes (aqueous solutions) are regulated by a number of factors [131-133] e.g. in the interactions between gypsum and salt solutions [134], the mechanism is basically controlled by the tendency of the cations in solution to form insoluble phases in the presence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Interactions of calcium carbonate mineral in electrolyte solution have been studied [135]. The interaction process between carbonate and electrolyte has been shown to occur primarily on the surface of lattice. Calcium carbonate in the precipitated form and freed from water by heating at 150°C , is used where mild adsorbent is required [91]. Several authors [136-138] studied the adsorption of phosphate and calcite. Calcium carbonate is also an important soil constituent as well as a frequently used soil amendment. The precipitated form of calcium carbonate has been taken as adsorbent for the study of molybdate adsorption [26].

In industrial as in laboratory practice decolorization is often carried out by adsorption as a purification step preparatory to the isolation of a desired product. Besides one of the largest

uses of charcoal in decolorizing sugar sirup as a step in preparing pure crystals [139]. It is also used in water purification industry [48,140]. Extremely large quantities of fuller's earth and other adsorbents are used in purifying petroleum products [51]. In the laboratory adsorption is used to remove impurities, especially those which may inhibit crystallization or produce foaming, and to produce a clear liquid preparatory to distillation or other manipulations [141]. Decolorizing agents are not to be thought of as chemically inert. The catalytic properties of charcoal and other adsorbents have been reported [48,142,143]. It is quite likely that many decolorizations are not purifications in the sense that they might at first appear to be. Some charcoals are known to possess strong reducing action-possibly because of adsorbed carbon monoxide. Others are actually oxidizing agents, perhaps through the agency of adsorbed oxygen.

The adsorption of chlorine on Ag(III) surface has been found to be efficient [144,145]. The formation of a surface iodide on Ni (100) & adsorption of Iodine at low temperatures, has been studied [146]. Bulk halide formation in UHV appears to be sensitive to

substrate crystallography. Both chloride [147] and iodide [148] are formed on Au (III) but no bromide formation occurs on Au [149]. The adsorption and reaction of I_2 and CH_3I with uranium monocarbide surface [150] have been studied. The adsorption of I_2 on UC occurs via a dissociative/oxidation process.

The interaction of dyes with metal hydrous oxide sols and gels have been studied by number of workers [151-156]. For adsorption of alizarin sulphonic acid, methyl orange and methylene blue, the adsorbents namely silicic acid gel, ferric oxide and alumina gel were taken [157]. Adsorption of dyes by insoluble salts and oxides has been studied, mostly from the stand point of the determination [158-160] of adsorption isotherm and related quantities e.g. surface area, coverage factor, particle size etc. The rate of the dyes methylene blue, crystal violet, malachite green and rhodamine B on silica gel and graphite from pure and mixed adsorbents has been studied [106]. The process was found to follow the first order kinetics. The amount adsorbed and the rate of adsorption were seen to depend on temperature, pH and concentration of the solution. Adsorption for a dye from mixed adsorbates was found to be lesser as

compared to that from a single adsorbate solution of the same concentration. The adsorption of cationic dyes, although believed to be primarily an exchange reaction [161], was dependent upon various factors such as molecular size, molecular geometry of the sorbate [162], dye-dye interaction [163] as well as the surface characteristics of the solvent [164,165]. Studies on the adsorption and desorption of methylene blue on and from vermiculite & asbestos have been done [166].

Only a few studies were carried out on the adsorption of dyes over inorganic solids. The adsorption characteristics of a range cationic dyes have been studied over alkaline chromatographic alumina powder [153]. The mechanism of various azo dyes on chromatographic alumina has been studied using spectrophotometric technique [167]. The adsorption studies over various hydrous ferric oxide samples were carried out by the dye crystal violet [168]. The adsorption properties were changed when excess or deficient amount of alkali was used in precipitating the adsorbent. The adsorption increased with increase in concentration of dye and also with rise in temperature [169].

Clays are known to adsorb basic dye stuffs from aqueous solutions. Reciprocal Langmuir plots are generally linear, indicating a monolayer adsorption of these dyes [170]. This adsorbing ability of clay minerals is attributed to an ion exchange process. But many clays, particularly of the swelling type viz. bentonites, are found to adsorb dye molecules well in excess of their respective exchange capacities. Various explanations for this behaviour have been proposed amongst which one is based on aggregation of dye molecules [171,172]. An evidence of such aggregation follows from an examination of the metachromatic shift in the spectrum exhibited by certain dyes [171-174], when sorbed on surfaces of colloidal particles. Coven and Weissbein [175] provided electron microscopic evidence for the dye-association on textile materials.

The adsorption per gram for a given solid, increases with an increase in its accessible surface area. The accessible area, in turn, for a given particle size depends upon the size and distribution of pores within the solid adsorbent. Since the adsorbate in a solution must reach the inner surface of a porous adsorbent by diffusion through capillaries filled with solvent, the amount of

adsorption in any given time will depend on the nature of the pores and capillaries [44]. The adsorption character of the adsorbents is dependent on the specific surface area and the pore volumes [7,10,11,176]. However the relationship between the surface chemical structure and the adsorption character of the adsorbents has not been studied very often [8,9]. The particle size of a powder is related to its external surface area per gram, is obvious, the finer the powder the greater the external area. Indeed for an ordinary ground up or broken up solid, it is difficult even to specify the particle size in simple terms, desirable though such specification is for control of such industrial processes as grinding and sieving [177].

Bruns [178] prepared a sugar charcoal by cooking sugar and activating it at 1000°C in the presence of hydrogen. He studied the effect of reduction of particle size of the adsorbent on the adsorption from 0.01 N solution in water of the fatty acids from 1 to 6 carbon atoms in chain length. Upon reduction in size of the charcoal particles the adsorption of the higher members of the fatty acid series increased more than that of the lower members. Because of this Bruns was able, from a charcoal which showed reversal of

Traube's rule, to obtain through reduction in particle size a charcoal which followed Traube's rule. According to Bruns this behaviour showed that the reversal of Traube's rule was due to the presence of pores, which were not accessible to molecules with large volume, and which were opened by mechanical partial-size reduction of the charcoal. This supported the "ultraporosity theory" of the cause of reversal of Traube's rule. On the other hand, Krczil [179] found that there was no increase in adsorptive power over the starting material when de-ashed sugar charcoal of particle size 0.2 to 0.1 mm was reduced to particle sizes less than 0.05 mm. The adsorption was tested on fatty acids from their 0.01 N aqueous solution. There were evident some difference in behaviour with different methods of activation, and so the reversal of Traube's rule with change in particle size observed by others must, he felt, be laid to some factors already present in the charcoal due to its pretreatment. From the various studies it was concluded [180] that a "large surface area" was not the sole requirement for a useful adsorbent. There is needed a large surface area accessible to the adsorptive in question as well as a preferential ability to take up the adsorptive. These requirements are important in the evaluation of adsorbents. The

influence of particle size [25] does not greatly influence the capacity of metal sorption.

Although the extent of adsorption increases (to the point of saturation of the adsorbent) with increase in concentration, the increase is relatively less at the higher concentrations [181]. This effect is more noticeable the more curved is the isotherm, so that the advantage gained may even be negligible. Also, if the coloured impurities are strongly adsorbed and the desired product weakly, so that the isotherm of the former is strongly curved compared with that of the latter, then adsorption of product may be improved by increased concentration relative to adsorption of impurities.

Adsorption is an exothermic process and increases with the decrease of temperature [182]. Takeo Asakawa and Keizo Ogine [183] have measured the effect of temperature on adsorption for the adsorption of phenol in aqueous solutions. Patel et al [184] determined the composite adsorption isotherm of cyclohexane - C_6H_6 and C_6H_6 -dioxane mixtures on Al_2O_3 at 20,30 and 40°C. The adsorption data were used for calculating the surface activity

co-effects at different temperatures and from the latter excess surface entropy values were derived. An increase in temperature is seen to increase the rate of adsorption of dyes on the two adsorbents [106], thus due to increase in temperature from 35 to 40°C, k enhances from 0.480 to 0.503 per minute in the adsorption of methylene blue on silica gel. The corresponding values of graphite are 0.119 & 0.216 per minute. Thakur and Das [26] have studied the adsorption of molybdate on precipitated phosphates of Alumina (III), Iron (III) and Calcium carbonate, at two temperature viz 20 and 40°C. A decrease of temperature favours adsorption of molybdate.

The data for the adsorption of dimethoate on three clay minerals and two soils at 15 & 25°C have been plotted [100]. It was seen that the amount of insecticide adsorbed on all clay mineral and soil decreased with the rise of temperature. Polymer adsorption is markedly dependent on the solvent, usually it is strongest from a "poor" solvent and vice versa. Sometimes the adsorption increases with temperature that is entropy rather than energy controlled, suggesting solvent release on adsorption [185,186].

Sorption - desorption behaviour of three oxyanions (MnO_4^- , CrO_4^{2-} and VO_3^-) on chromatographic alumina pretreated with HNO_3 has been described [187]. The sorption was found to be pH dependent and has maximum at surface pH values of 3.5 (MnO_4^-) 2.5 (VO_3^-) and 2.0 (CrO_4^{2-}). The affinity of MnO_4^- and CrO_4^{2-} was almost negligible at surface pH values of 5.5 or more. However VO_3^- showed affinity for the substrate in the pH range 5.0 to 8.8. The monovalent anion appeared to be sorbed, primarily, via electrostatic interaction with the surface sites created by the acid treatment. The CrO_4^{2-} appeared to involve ion exchange and weak chemical interactions, mixtures of oxyanions were separated (binary and ternary) by column chromatography using inorganic electrolytes as eluents.

Mac Naughton [188] studied the effect of pH on the adsorption of CrO_4^{2-} from water on different oxides. He reported that the anion was adsorbed at low pH and adsorption was zero at high pH. Yosida and Kamega [189] observed that Cr(vi) was adsorbed quantitatively on activated carbon at pH 3.5-6.5 and the adsorption appears to be involve binding of the anion to positive sites in the activated

carbon. Sai et al [190] have also found pH dependent adsorption behaviour of Cr(vi). Shimiza et al [191] noticed a decrease in adsorption of Cr(vi) on silk fibres from aqueous solution (6h. 25°C) with increasing pH. Fushimi et al [119] have reported that the pH of the solution has a significant effect on the adsorption of metal ions.

It is reported that high temperature activation produces a charcoal which may be quite organophilic in its properties, while low-temperature activation, particularly in the presence of a strongly oxidising atmosphere, produces a hydrophilic charcoal which may be made very hydrophilic indeed. If charcoal is to be used with oxidation-sensitive substances, it may be advisable to heat it to a high temperature and cool it in an inert atmosphere [192]. In some applications charcoals need to be degassed before they show their highest capacity. The solvent, in such cases, seems unable to penetrate the air or gas filled capillaries [193]. In the activation of charcoal very high temperature was avoided, since above about 1100°C graphitization, with loss in activity, takes place. In the activation of alumina, the temperature was not exceeded to 200°C[194]

The alumina dried at this temperature still contains some moisture (around 8 percent). To drive off all the moisture requires a temperature so-high as to cause sintering and loss of activity of the porous adsorbent.

Reproducible activation of silica gel has been discussed by Bartell and Almy [195]. They have suggested that gel should not be heated above 300°C. With Bartell and Almy's sample of gel the maximum activity was produced by heating two hours at 300°C. Adsorbed water was still present and could be driven off at higher temperatures, but it appeared that under these conditions the gel structure collapsed. At any rate, the activity of the gel decreased. Mair [196] reactivated silica gel after using it to adsorb hydrocarbons by heating it to 180 to 200°C in a slow stream of inert gas. Much work has been done on the activation of adsorbents by coating them with metals [197], fatty acids and other substances [198]. Most adsorbents can be recovered by washing off the adsorbed material and reactivating the adsorbent [199]. A good bone char may withstand some 200 revivifications before being discarded [51].

Owing to the high cost of activated carbon, other substances have recently been used as adsorbents. One of them is new, mineral-carbonic adsorbent produced from wastes. Studies on usability of that sorbent for dye house waste water treatment were conducted [200], Dusty mineral-carbonic adsorbent is produced from used up montmorillonite clays left over after refining of petroleum products. These clays were treated with concentrated sulfuric acid at the increased temperature. The sorbent having a coating of carbonized organic compounds on the mineral aluminosilicate skeleton was obtained as a product of this process. The adsorption of a dye stuff, telon blue (Acid Blue 25) on fuller's earth and astrazone blue on to fired clay has been studied [201]. An intraparticle diffusion rate parameter has been defined characteristic of the rate of diffusion after the early state of the adsorption. The rate parameters have also been determined for a number of variables including adsorbent mass, initial dye concentrations and particle size.

Experiments were conducted to evaluate adsorption capacity of granular activated carbon Nuchar C-190 for the removal of Y-hexachlorocyclohexane (Lindane) from drinking water at microlevels.

The effect of pH, concentration of lindane carbon dose and contact period have been studied [202]. It was observed that adsorption controlled by rate of diffusion in the pores of carbon is independent of pH and concentration. A carbon dose twice the weight of lindane, removed 99.5 percent of 2 mg/l lindane in 2 hours contact at pH 7.0. Adsorption of glycolic and lactic acid from aq. solutions on surface of activated charcoal at 30°C was accomplished by a titrametric method [203]. The rate of adsorption of glycolic and on activated charcoal was greater than lactic acid. Nature and number of functional groups attached to the side chain influence the concentrations involved in the Langmuir ($1/a$, $1/ab$) and Freundlich ($\log a, 1/n$) isotherms alongwith the side chain.

Cobalt (II) ions were adsorbed on to silica gel from solutions containing metal ions and organic ligands [204]. The treatment of organically contaminated industrial wastes by cement - based stabilization/solidification has, in the past, been restricted by the detrimental effect of organic compounds on cement hydration. Montgomery et al [205] investigated the use of organophilic clays as adsorbents for the organic components of industrial wastes prior to

conventional cement - based solidification. Three industrial wastes containing between 2-12 percent organic carbon and trace heavy metal contamination were treated with a free quarternary ammonium salt exchanged clay. The organic component of all three wastes was well adsorbed by the clay. Solidification of the waste/clay mixes produced a monolithic mass with adequate strength and very low leaching of either the organic compounds or the metals.

A systematic investigation of the equilibrium absorption and rate of adsorption of hydroxyethyl cellulose (HEC), hydroxypropyl methyl cellulose (HPMC) and polyvinyl alcohol (PVOH) was undertaken [206] with clay, mica, talc and limestone. For all 4 solids, the amount of polymer adsorbed was greatest for PVOH and least for HEC. For each polymeric species, the amount of polymer adsorbed at equilibrium decreased in the order clay, talc, mica and limestone. Adsorption isotherms for the adsorption of 3,6-diaminoacridine on kaolin clay showed that the dye molecules penetrate into the interlayer space of the aluminosilicate layer of the clay, while in the case of alumina the dye molecules cover only the surface. Adsorption spectral studies of dye adsorbed on kaolin and bentonite

at lower dye concentrations indicated that 3,6-diaminoacridine exists as a monomer in the adsorbed state. The emission of dye adsorbed on clays was quenched completely even in dilute solution [207].

The adsorption properties of tea treated by formaldehyde for Sr^{2+} in water were studied [208]. The adsorption equilibrium concentration (k) and the maximum adsorption quantity could be obtained from the Langmuir equation. The adsorption of Sr^{2+} by treated, untreated reused tea and by active carbon were compared [208]. The tea after adsorbing Sr^{2+} could be reused by washing with 0.05 M HCl. Anon [209] has investigated the charred waste obtained on treatment of the bark of a tree (*Terminalia tomentosa*, cambreatacea) with sulphuric acid for the manufacture of oxalic acid, as a good adsorbent for toxic ions (Pb^{2+} , Hg^{2+} , F^- and $\text{Cr}_2\text{O}_7^{2-}$) and dyes.

The adsorption of phenols (phOH, P-nitrophenol, salicylic acid, p-amino phenol) from aqueous solutions by various types of carbon fibers derived from hydrate cellulose or polyacrylonitrile was studied and conditions for adsorbent regeneration were established [210]. The Dubinin Astakhov equation was obeyed, but the adsorption mechanism was dependent on the polarized carbon fiber structure and

Surface properties. Sorption capacities was regenerated by electro chemical treatment. Surfactant adsorption and the enthalpy of adsorption were evaluated by flow adsorption colorimetry [211]. This technique permitted the simultaneous determination of both the quantity and the enthalpy of adsorption. Temperature, salinity, surfactant type and the wettability of the adsorbent surface all have an effect on the amount of and the enthalpy of adsorption. In general there has been a decrease in adsorption as temperature increases and an increase as salinity increases, upto a maximum. Similarly, the molar enthalpy of adsorption has increased with increasing temperature and decreased with increasing salinity. The molar enthalpy of adsorption for all surfactant types was higher for oil-wet than for water-wet material. A Langmuir isotherm adequately described the adsorption of cationic surfactant on an oil-wet surface for all temperatures and salinities.

M A T E R I A L S A N D M E T H O D S

MATERIALS AND METHODS

Before proceeding for detailed studies, it was thought worthwhile to observe the adsorptive activities of the shells of *Unio* & *Pila*, a preliminary investigation was undertaken. The shells were collected from a local river. They were washed, dried, ground & sieved to 100 mesh and activated. The activated powders of the shells were taken as adsorbents in aqueous and alcoholic media. The aqueous medium contained 5 percent potassium iodide (KI). 50 ml. of each of 0.02 M, 0.15 M and 0.01 M aqueous and alcoholic solution of Iodine were separately taken and tested for adsorption on 2 g samples of the powdered adsorbents at 25°C. After 2 hours contact period, the solutions were filtered and the equilibrium concentration of Iodine in the filtrate was determined by titration against Sodium thiosulphate solution.

Encouraged from the results of preliminary work, the detailed studies were planned. It is needless to emphasise the abundance and easy availability of vast natural resources in the sphere of flora and fauna. The hard protective shells, the creatives of water dwelling animals : *Unio* & *Pila* conform to this category too.

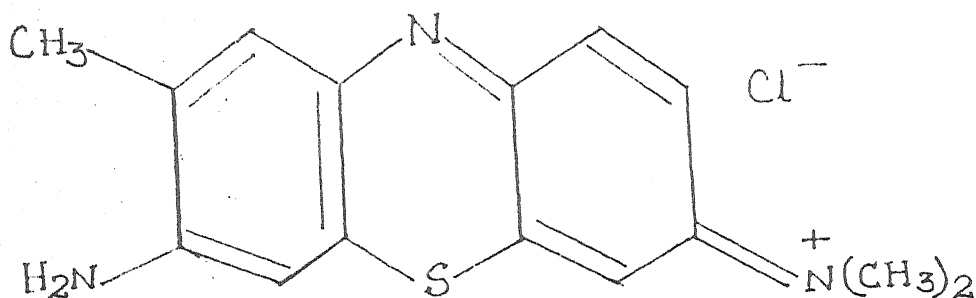
The fresh water river PAHOOT, originating from Jhansi district, almost the demarcating line between Uttar Pradesh and Madhya Pradesh, flows up to Jalaun district where it falls in the pious water of legendary river YAMUNA, together with other three rivers. The confluence of these five rivers is known as PANCHNADA, attracts the large gathering of far and near people, to take holy dip. The great suntemple of Balaji at village Unnao (District - Datia, Madhya Pradesh) is situated on the bank of Pahoot, where pilgrims offer prayers only after taking dip in its sacred water.

The shells of Unio and Pila are found in plenty in and around the Pahoot, throughout its whole stretch. The river leaves a wide area along its two sides. The shells were easily collected from the various places of this river, in Jalaun & Jhansi districts (Uttar Pradesh) and Datia district (Madhya Pradesh). The shells collected were of white & pink colour and ranged from 1 cm. to 5 cm. in size. The shells were gently washed with fresh water repeatedly to make them free from dust & sand and then they were passed through the process of boiling with water in order to remove the sticky materials. The shells were dried completely in sunlight. They were

broken to small pieces by mortar and pestle and then ground to fine powder. Powders of both the shells were passed through 120 mesh and 80 mesh sieves. The uniform fractions of all these powders were activated by heating in muffle furnace at 400°C for 4 hours. The activated powders were stored in marked, stoppered glass bottles which were kept in a desiccator at room temperature, to avoid the contact with moisture.

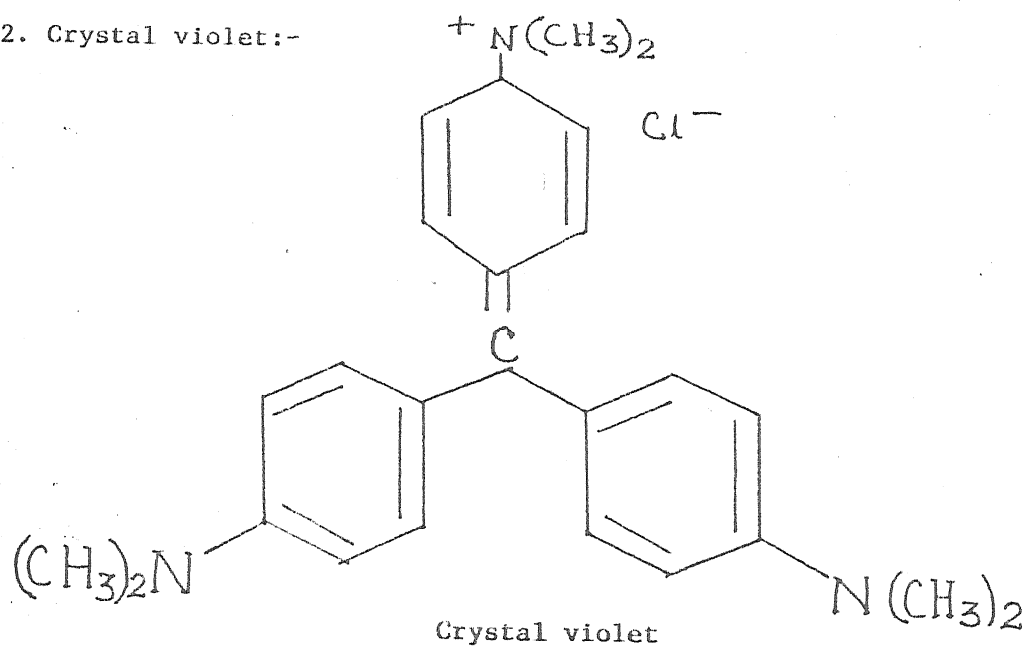
The adsorptive capacities of these powders as adsorbents were studied with the solution of chemically pure grade colouring materials (without further purification) & coloured effluents collected from different textile dyeing industries. The following colouring materials were used as adsorbates:-

1. Toluidine blue:

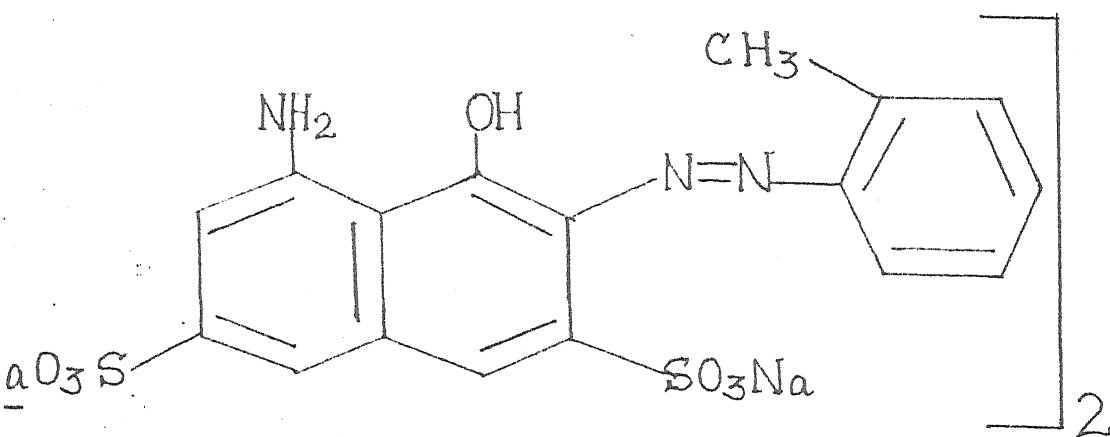


Toluidine blue

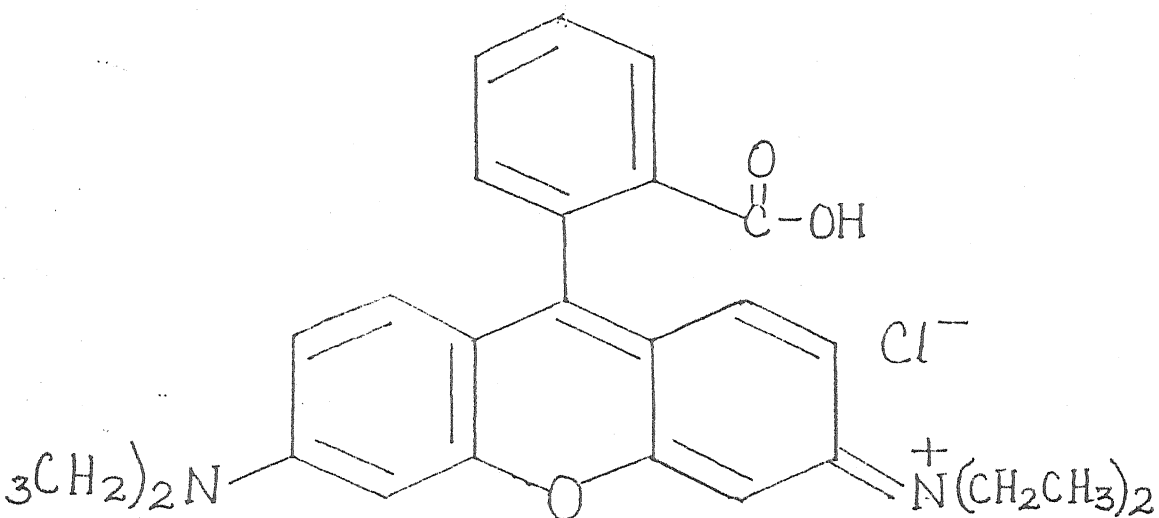
2. Crystal violet:-



3. Trypsan blue:-

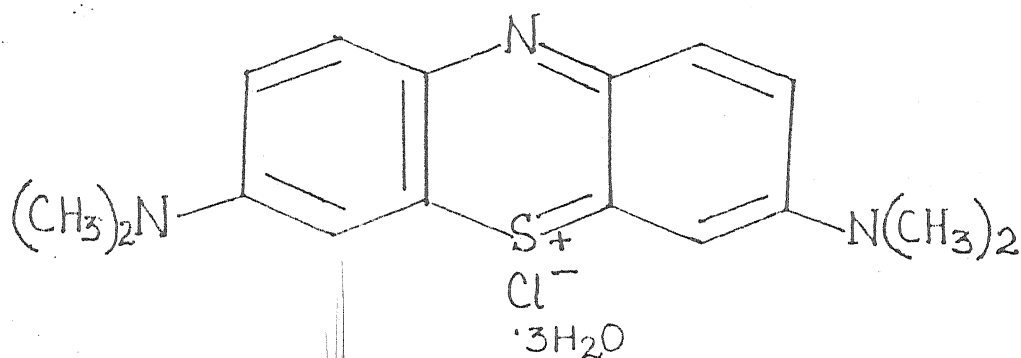


4. Rhodamine B:-



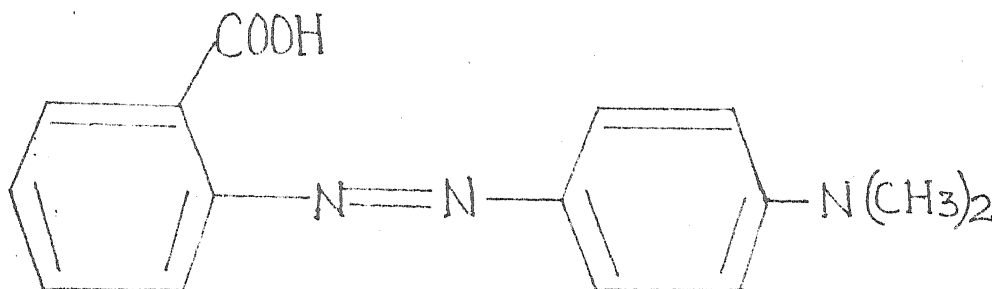
Rhodamine B

5. Methylene blue:-



Methylene blue

6. Methyl red:-



Methyl red

The aforesaid solid adsorbates were weighed accurately and their stock solutions of 1000 $\mu\text{g/L}$ were prepared in warm double distilled water. All the solutions contained 10 percent ethyl alcohol to facilitate the solubilities of the adsorbates in water. The stock solutions were kept overnight to get stabilise and acquire room temperature. The stock solutions were covered with a double layer of black cloth to protect them from the effect of sunlight. These solutions were diluted to 800 $\mu\text{g/L}$, 600 $\mu\text{g/L}$, 400 $\mu\text{g/L}$ & 200 $\mu\text{g/L}$

respectively by addition of water. 20 ml each of the above mentioned test solutions were pipetted out in order to make two sets in duplicate, into a series of numbered and stoppered pirex glass conical falsks, for comparative study of Unio & Pila shell powders (particle size : 120 mesh) at 10°C. Similar series of sets were taken for adsorption experiments at 25°C.

500 mg activated powder of 120 mesh of each of the adsorbents was weighed in stoppered glass tubes and put into numbered conical flasks of the series containing the adsorbate solutions. The flasks of duplicate series were placed systematically in thermostating condition in B.O.D. incubator at 10°C ($\pm 1^\circ\text{C}$) and another series in duplicate at 25°C ($\pm 1^\circ\text{C}$) for 2 hours. The flasks were shaken serially at frequent intervals for ascertaining proper contacts of all the particles of adsorbents with adsorbates. Immediately after incubation the equilibrated solutions were decanted into the graduated and numbered centrifuging tubes and centrifuged for 10 minutes at 10,000 r.p.m.. The supernatant solutions were taken into the clean tube serially and amounts of adsorbates, adsorbed were calculated from the difference in initial

and the equilibrium concentrations of these solutions, measured spectrophotomerically by SPECTONIC-20 colorimeter.

With the rise of living standard and population explosion, the problem of pollution has been creating disturbances in the environmental equilibrium. Chemical pollution in air, water and soil is becoming a challenging task to the mankind. Untreated industrial wastes discharged into lakes and streams result in serious problems of water pollution. Few unwanted dissolved minerals cause hard water problems for industrial and municipal water supplies. Biological activity of the streams may be altered by toxic chemicals and many chemicals cause to rise the acidity and alkalinity in reaction with water, to the point where the water becomes corrosive; thus living organisms are killed. Chemicals which need more oxygen, give room to the problem of deoxygenation. Water purification represents the main, well established and refined technology. Possibly the most recent technology that has and will contribute in the future to lessening water pollution is that of water reuse: the recycling and in-plant treatment of water for manufacturing and processing purposes.

The industries discharge untreated water on land and in natural streams. The textile industries are one of them. The waste waters of varying colours come out of the textile industries. Many people who perform the dyeing works at small and large scale, manually, allow the untreated water, containing the different dyes, to flow in the drains which ultimately go to the rivers, lakes and ponds, resulting to water pollution. Dyes are the major constituents of these colouring matters of effluents. The samples of effluents of six open drains of local textile dyeing industries were collected. The effluents were of Red, Violet, Sky blue, Yellow, Green & Orange in colour respectively. The samples were dark coloured and foul smelling. They were filtered through whatman no.40 filter paper. The filterates were stored in stoppered and marked measuring flasks. The filtrates of these flasks were termed as stock solutions. They were kept for overnight at room temperature and covered with a double layer of black cloth to prevent them from the effect of sunlight. Double distilled water was added with these solutions for diluting them to 20.0, 40.0, 60.0 & 80.0 percent respectively. For performing comparative adsorption experiments of Unio & Pila shell powders at

temperature of 10°C , 20 ml. of each of the solutions were pipetted out into a stoppered and numbered conical flasks in 2 sets of duplicate series. For adsorption studies at a temperature of 25°C , the series of sets were arranged similarly. In stoppered glass tubes, 500 mg activated powders of 120 mesh of each of the adsorbents were weighed and put into each flasks of the series. The serially arranged flasks were placed in themostating conditions for incubation at 10°C ($\pm 1^{\circ}\text{C}$) and 25°C ($\pm 1^{\circ}\text{C}$) in B.O.D. incubator for 2 hours. To ascertain the proper contacts of the particles of adsorbents with the solutions, the flasks were shaken simultaneously at frequent intervals. The graduated and numbered centrifuging tubes were taken and just after incubation, the equilibrated solutions were decanted into them. These solutions were centrifuged at 10,000 r.p.m. for 10 minutes. The supernatant solutions were taken into the clean tubes and the amounts of dyes adsorbed were calculated by difference of their initial and final concentrations, measured spectrophotometrically by SPECTONIC - 20.

Adsorption is a surface phenomenon, depends upon the surface area of the adsorbents, at the given time, temperature & pressure.

The extent of adsorption for the solid adsorbents increase with an increase in their accessible surface area. The external area will be greater for finer powder of the adsorbent. The size and distribution of pores within the solid adsorbents are responsible for accessible surface area for a given particle size. When the solid adsorbents are crushed to smaller particles, new pores are opened. By diffusion through capillaries filled with the solvent, the adsorbates in the solutions reach the inner surface of the porous adsorbents, thus the amount of adsorbates, adsorbed will be dependent on the nature of pores and capillaries of the adsorbents. Obviously, the size of particles of the adsorbents has a significant relation with their external area for their given quantity. To assess the effectiveness of particle size of Unio & Pila shells, the adsorption experiments were undertaken. For this purpose 500 mg activated powders of particle size 80 mesh of Unio & Pila shells were weighed in stoppered glass tubes. All the sets of flasks were arranged in the similar ways as was done for conducting the studies with 120 mesh powders. The test solutions of adsorbates, viz. Dyes and Effluents were also taken likewise and were treated in the same manners and the experiments

were carried out at 10°C & 25°C. For calculating the amounts of dyes adsorbed, the earlier procedure was adopted.

Bailey et.al. [212] have determined partial molar free energy of macroscopically homogeneous open thermodynamic system [213] by means of expression:

$$-\bar{G} = RT \ln C_e/C_o$$

Where; R = Molar gas constant

T = Absolute temperature

C_e = Equilibrium concentration and;

C_o = Initial concentration of the adsorbate solution prior to adsorption.

By using the above relationship the values of partial molar free energy were obtained and arranged in the tabular form.

The values of adsorptions in terms of percentage were calculated and recorded in the tables. A graphical study was also undertaken by plotting the amount of different dye adsorbed per 500 mg of each of the adsorbents against equilibrium concentrations at 10°C and 25°C for varying particle size.

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OBSERVATIONS AND RESULTS

OBSERVATIONS AND RESULTS

Adsorption of Iodine:

In the preliminary study to test the adsorptive capacities of the shells of *Unio* and *Pila*, there was significant adsorption of Iodine by both the shells (vide appendix - 1). The investigations conducted titrimetrically in aqueous and alcoholic media were confirmed spectrophotometrically.

ADSORPTION OF DYES ON UNIO SHELLS

Toluidine blue:

The adsorptions of Toluidine blue on *Unio* shells (particle size: 120 mesh) at temperature 10°C were 65.0, 60.0, 55.0, 50.0 & 44.0, percent for increasing initial dye concentrations (Table 1 & 1a). The nature of curve (Fig. 1) showed rise in the amount of dye adsorbed on increase in dye concentrations. The respective partial molar free energy values were 594.19, 518.62, 451.95, 392.32 & 328.17 calories/mole. At temperature 25°C the percent adsorptions were 55.0, 55.0, 46.66, 45.0 & 40.0 and partial molar free energy values were 475.91, 475.91, 374.65, 356.31 & 304.45 calories/mole respectively in the same order of initial concentrations of the adsorbate.

Table - 1. Adsorption of dyes on Unio Shells (Particle size: 120 mesh)

Initial dye concentration ($1 \times 10^4 \mu\text{g/L}$)	Temperature 10°C		Temperature 25°C	
	Equilibrium dye concentration ($1 \times 10^4 \mu\text{g/L}$)	Amount of dye adsorbed ($\mu\text{g}/0.5\text{g}$)	Equilibrium dye concentration ($1 \times 10^4 \mu\text{g/L}$)	Amount of dye adsorbed ($\mu\text{g}/0.5\text{g}$)

Toluidine blue:

200	70	130	90	110
400	160	240	180	220
600	270	330	320	280
800	400	400	440	360
1000	560	440	600	400

Crystal violet:

200	10	190	30	170
400	70	330	90	310
600	110	490	170	430
800	220	580	240	560
1000	350	650	380	620

Trypsan blue:

200	60	140	90	110
400	180	220	210	190
600	310	290	340	260
800	490	310	520	280
1000	670	330	700	300

Continuation of Table - 1.

Rhodamine B:

200		100		100		120		80
400		230		170		260		140
600		410		190		440		160
800		620		180		610		160
1000		810		190		840		160

Methylene blue:

200		20		180		40		160
400		100		300		130		270
600		180		420		210		390
800		290		510		310		490
1000		430		570		480		520

Methyl red:

200		0		200		10		120
400		30		370		60		340
600		80		520		110		430
800		150		650		180		620
1000		260		740		280		720

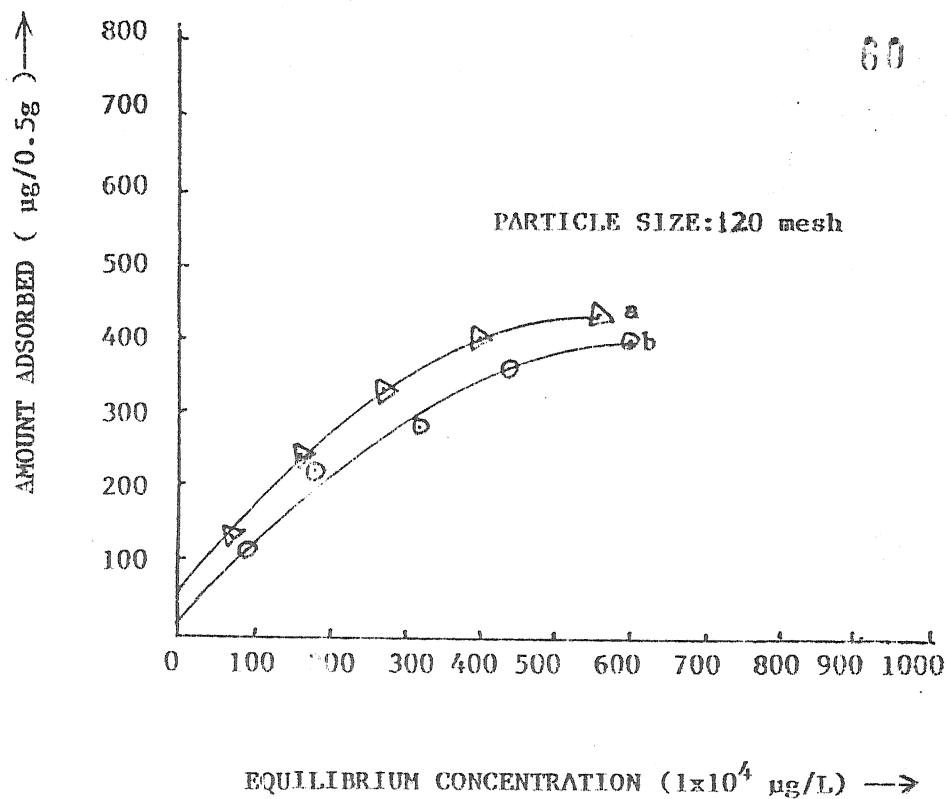
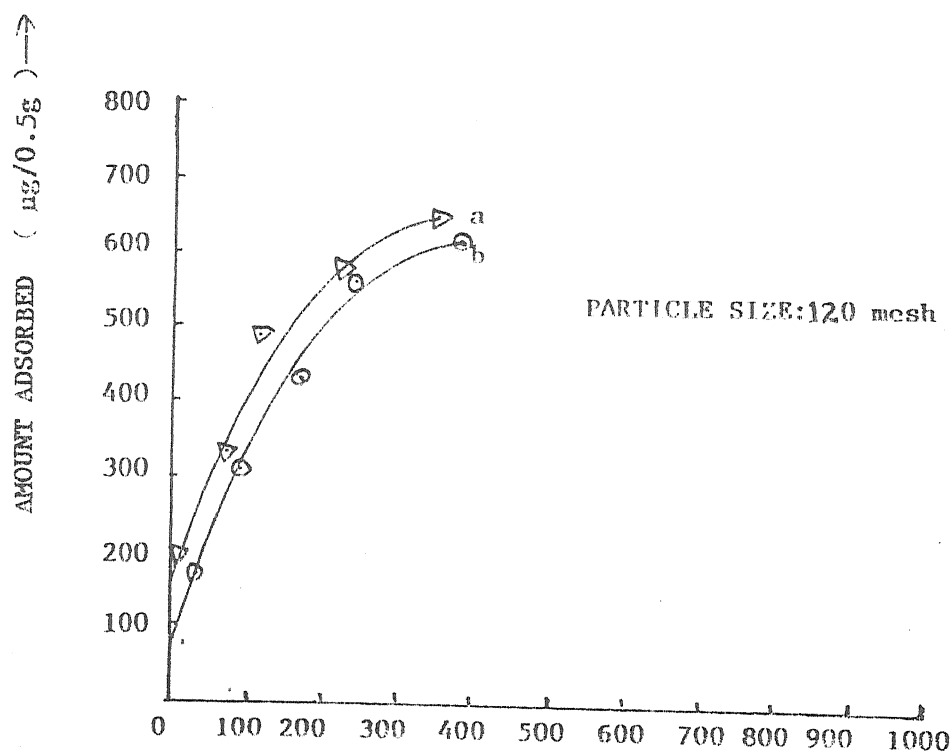


Fig.1: Adsorption isotherms for Toluidine blue on Unio Shell (a) 10 and (b) 25°



of curve was similar as above.

On particle size 80 mesh (Temperature : 10°C) the percent adsorptions were 60.0, 52.5, 45.0, 42.5 & 36.0 percent and partial molar free energy values were 518.62, 421.35, 338.37, 313.21 & 252.59 *Cal./mole* (Table 2 & 2a). At temperature 25°C the adsorptions were 50.0, 45.0, 40.0, 37.5 & 33.0 percent and the values calculated for partial molar free energy were 413.11, 356.31, 304.45, 280.12 & 238.68 *calories/mole*. The curves at both the temperatures showed an increase in the amount adsorbed on increase in concentrations (Fig.7)

Crystal violet:

At temperature 10°C , the adsorptions of Crystal violet on Unio shells (particle size: 120 mesh) were 95.0, 82.5, 81.66, 72.5 & 65.0 percent and the respective values of partial molar free energy were 1695.58, 986.52, 960.19, 730.69 & 594.19 *calories/mole* for increasing order of initial dye concentrations (Table 1 & 1a). The nature of curve showed an increase in the amount of dye adsorbed on increase in the concentrations (Fig. 2). At temperature 25°C the adsorptions were 85.0, 77.50, 71.66, 70.0 & 62.0 percent and their

Table 1 a. Adsorption of dyes on Unio Shells (Particle size: 120 mesh)

Initial dye concentration (1×10^4 ug/L)	TEMPERATURE 10°C			TEMPERATURE 25°C	
	Percent Adsorption	Partial molar free energy $-\bar{G}$ (Cals./Mole)		Percent Adsorption	Partial Molar free energy $-\bar{G}$ (Cals./mole)

Toluidine blue:

200	65.00	594.19	55.00	475.91
400	60.00	518.62	55.00	475.91
600	55.00	451.95	46.66	374.65
800	50.00	392.32	45.00	356.31
1000	44.00	328.17	40.00	304.45

Crystal violet:

200	95.00	1695.58	85.00	1130.68
400	82.50	986.52	77.50	889.02
600	81.66	960.19	71.66	751.63
800	72.50	730.69	70.00	717.56
1000	65.00	594.19	62.00	547.65

Trypsan blue:

200	70.00	681.44	55.00	475.91
400	55.00	451.95	47.50	384.03
600	48.33	373.76	43.33	338.51
800	38.75	277.45	35.00	256.74
1000	33.00	226.67	30.00	212.57

Continuation of table 1 a;

Rhodamine B:

200		50.00		392.32		40.00		304.45
400		42.50		313.21		35.00		256.74
600		31.66		215.51		26.66		184.85
800		22.50		144.26		20.00		132.99
1000		19.00		119.26		16.00		103.91

Methylene blue:

200		90.00		1303.26		80.00		959.22
400		75.00		784.64		67.50		669.86
600		70.00		681.44		65.00		625.69
800		63.75		574.33		61.25		563.03
1000		57.00		477.68		52.00		437.44

Methyl red:

200		100.00		3001.68		95.00		1785.45
400		92.50		1466.09		85.00		1130.68
600		86.66		1140.43		81.66		1011.08
800		81.25		947.47		77.50		889.02
1000		74.00		762.44		72.00		758.68

partial molar free energy values were 1130.68, 889.02, 751.63, 717.56 & 547.65 calories/mole respectively. The curve showed similar nature as above (Fig. 2).

At temperature 10°C, 80.0, 72.5, 70.0, 66.25 & 60.0 percent Crystal violet adsorbed on Unio shells (particle size :80 mesh) for increasing order of initial concentrations of dye and partial molar free energy values were 910.64, 730.69, 681.44, 614.78 & 518.62 calories/mole respectively (Table 2 & 2a). The percent adsorptions of Crystal violet at 25°C were 70.0, 65.0, 63.33, 60.0 & 57.0 and the corresponding partial molar free energy values were 717.56, 625.69, 597.96, 546.10 & 503.0 calories/mole. The nature of curve at 10°C & 25°C showed an increase in the amount of dye adsorbed on increase in the concentrations of Crystal violet (Fig.8).

Trypsan blue:

Adsorptions of Trypsan blue on 120 mesh Unio shells were 70.0, 55.0, 48.33, 38.75 & 33.0 percent at temperature 10°C for increasing initial dye concentrations and the corresponding values of partial molar free energy were 681.44, 451.95, 373.76, 277.45 &

Table - 2. Adsorption of dyes on Unio Shells (Particle size: 80 mesh)

Initial dye concentration ($1 \times 10^4 \mu\text{g/L}$)	Temperature 10°C		Temperature 25°C	
	Equilibrium	Amount of	Equilibrium	Amount of
	dye concent-	dye	dye concent-	dye
	ration	adsorbed	ration	adsorbed
	($1 \times 10^4 \mu\text{g/L}$)	($\mu\text{g}/0.5\text{g}$)	($1 \times 10^4 \mu\text{g/L}$)	($\mu\text{g}/0.5\text{g}$)

Toluidine blue:

200	80	120	100	100
400	190	210	220	180
600	330	270	360	240
800	460	340	500	300
1000	640	360	670	330

Crystal violet:

200	40	160	60	140
400	110	290	140	260
600	180	420	220	380
800	270	530	320	480
1000	400	600	430	570

Trypsan blue:

200	90	110	110	90
400	220	180	250	150
600	360	240	390	210
800	530	270	550	250
1000	720	280	750	250

Continuation of Table - 2.

Rhodamine B:

200		120		80		140		60
400		270		130		290		110
600		450		150		470		130
800		650		150		670		130
1000		850		150		870		130

Methylene blue:

200		30		170		50		150
400		110		290		150		250
600		230		370		250		350
800		340		460		370		430
1000		500		500		530		470

Methyl red:

200		10		190		30		170
400		60		340		80		320
600		120		480		160		440
800		200		600		230		570
1000		280		720		320		680

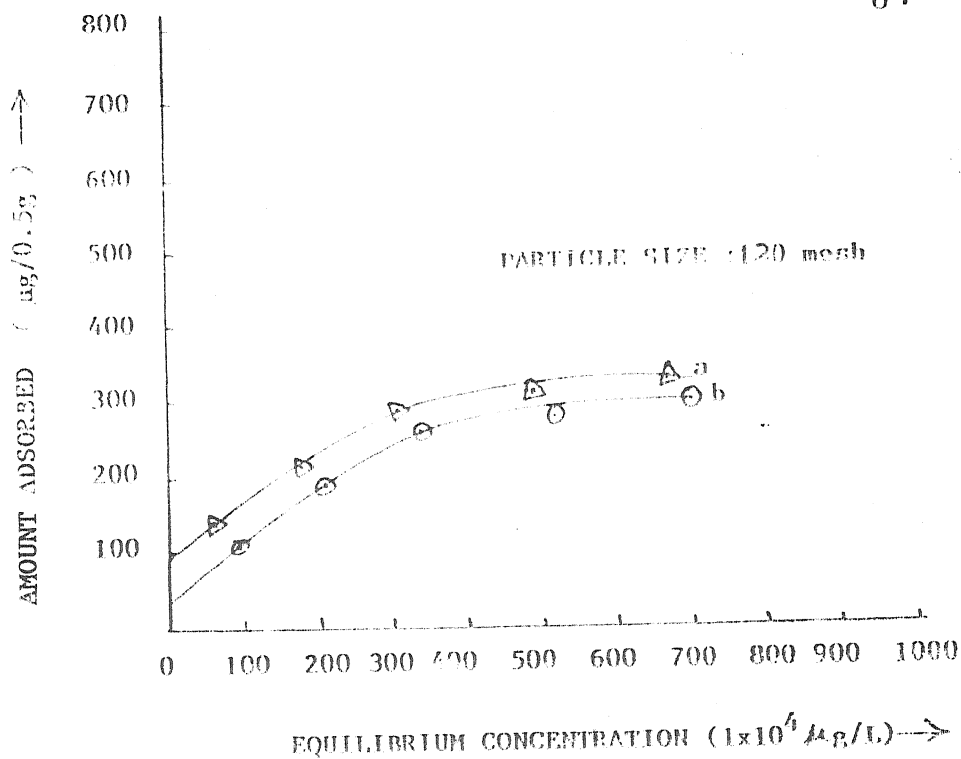


Fig. 3: Adsorption isotherms for Trypsin blue on Unio Shell (a) 10 and (b) 25°

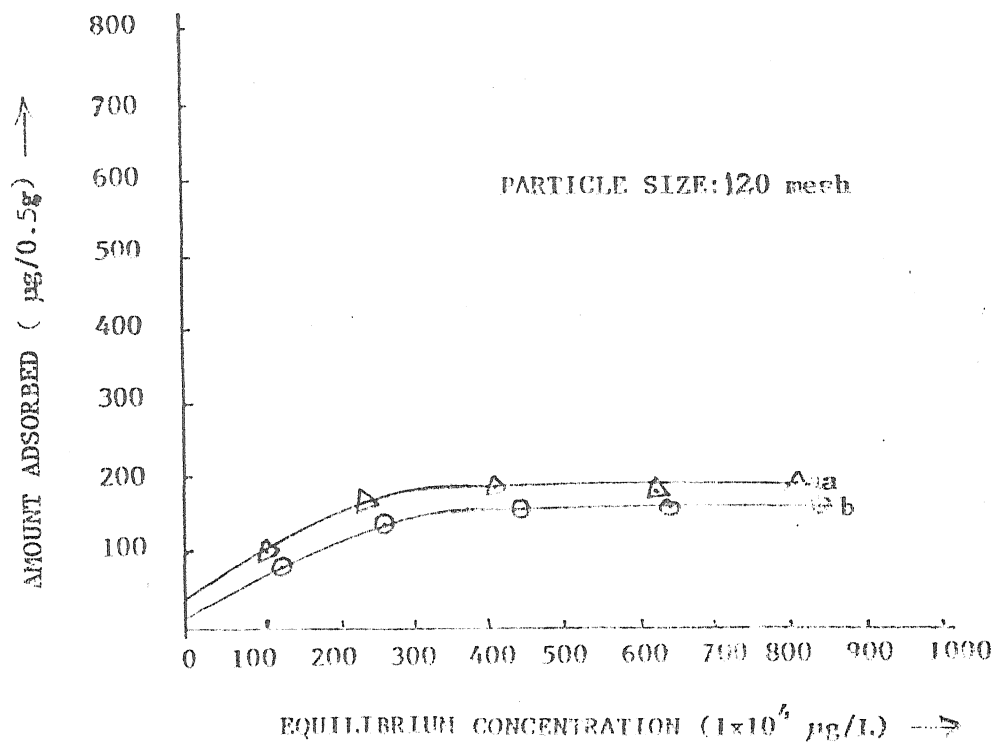


Fig. 4: Adsorption isotherms for Rhodamine B

226.67 calories/mole. At temperature 25°C the adsorptions were 55.0, 47.5, 43.33, 35.0 & 30.0 percent and the respective values of partial molar free energy were 475.91, 384.03, 338.51, 256.74 & 212.57 calories/mole (Table 1 & 1a). The curves showed an increase in the amount of Trypsan blue adsorbed on increasing concentrations at both the temperatures (Fig. 3).

The experiments with the particle size of 80 mesh, for increasing order of initial concentrations of Trypsan blue showed 55.0, 45.0, 40.0, 33.75 & 28.0 percent adsorptions at 10°C and the values calculated for partial molar free energy were 451.95, 338.37, 289.12, 233.04 & 185.93 calories/mole respectively. At 25°C the adsorptions were 45.0, 37.5, 35.0, 31.25 & 25.0 percent and the respective values of partial molar free energy were 356.31, 280.12, 256.74, 223.31 & 171.45 calories/mole (Table 2 & 2a). The nature of curves was similar as above (Fig. 9).

Rhodamine B:

The adsorptions of Rhodamine B on Unio shells (particle size :120 mesh) were 50.0, 42.5, 31.66, 22.5 & 19.0 percent at 10°C

Table 2 a: Adsorption of dyes on Unio shells (Particle size: 80 mesh)

Initial dye concentration (1×10^4 $\mu\text{g/L}$)	TEMPERATURE 10°C			TEMPERATURE 25°C	
	Percent	Partial Molar		Percent	Partial Molar
	Adsorption	free energy		Adsorption	free energy
		$-\bar{G}$ (Cals./Mole)			$-\bar{G}$ (Cals./Mole)

Toluidine blue :

200	60.00	518.62	50.00	413.11
400	52.50	421.35	45.00	356.31
600	45.00	338.37	40.00	304.45
800	42.50	313.21	37.50	280.12
1000	36.00	252.59	33.00	238.68

Crystal violet :

200	80.00	910.94	70.00	717.56
400	72.50	730.69	65.00	625.69
600	70.00	681.44	63.33	597.96
800	66.25	614.78	60.00	546.10
1000	60.00	518.62	57.00	503.00

Trypsan blue :

200	55.00	451.95	45.00	356.31
400	45.00	338.37	37.50	280.12
600	40.00	289.12	35.00	256.74
800	33.75	233.04	31.25	223.31
1000	28.00	185.93	25.00	171.45

Continuation of table 2 a:

Rhodamine B :

200		40.00		289.12		30.00		212.57
400		32.50		222.46		27.50		191.66
600		25.00		162.82		21.66		145.54
800		18.75		117.52		16.25		105.69
1000		15.00		91.98		13.00		83.00

Methylene blue:

200		85.00		1073.76		75.00		826.23
400		72.50		730.69		62.50		584.57
600		61.66		542.70		58.33		521.77
800		57.50		484.30		53.75		459.58
1000		50.00		392.32		47.00		378.38

Methyl red:

200		95.00		1695.58		85.00		1130.68
400		85.00		1073.76		80.00		959.22
600		80.00		910.94		73.33		787.76
800		75.00		784.64		71.25		742.93
1000		72.00		720.49		68.00		679.10

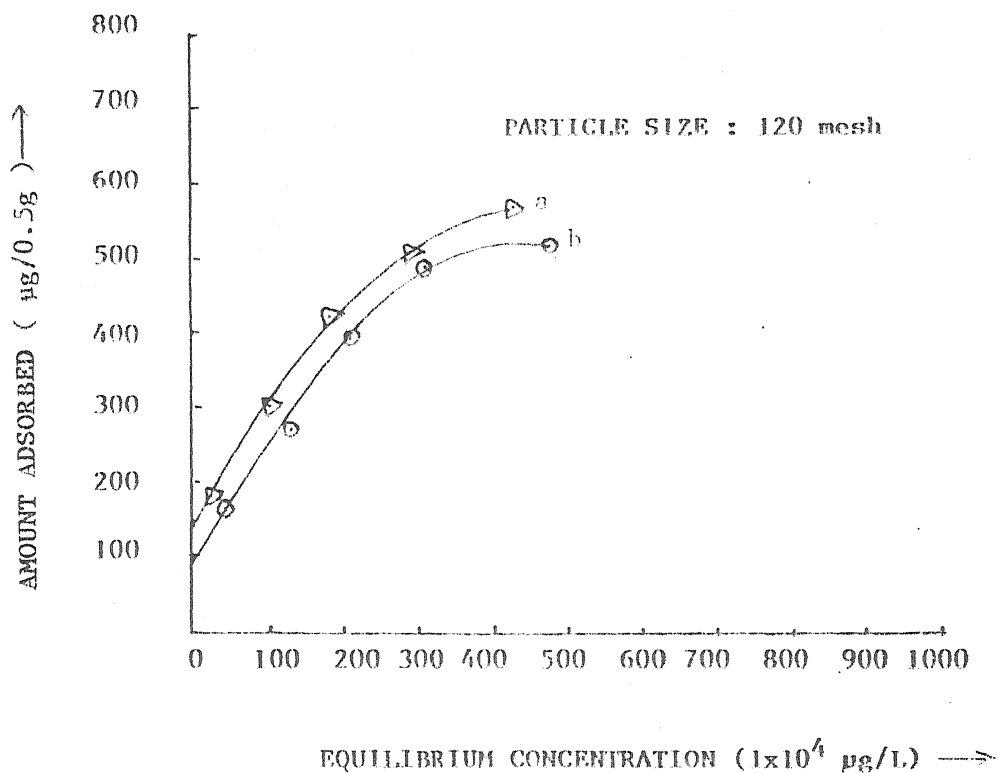


Fig.5: Adsorption isotherms for Methylene blue on Unio Shell (a) 10 and (b) 25°

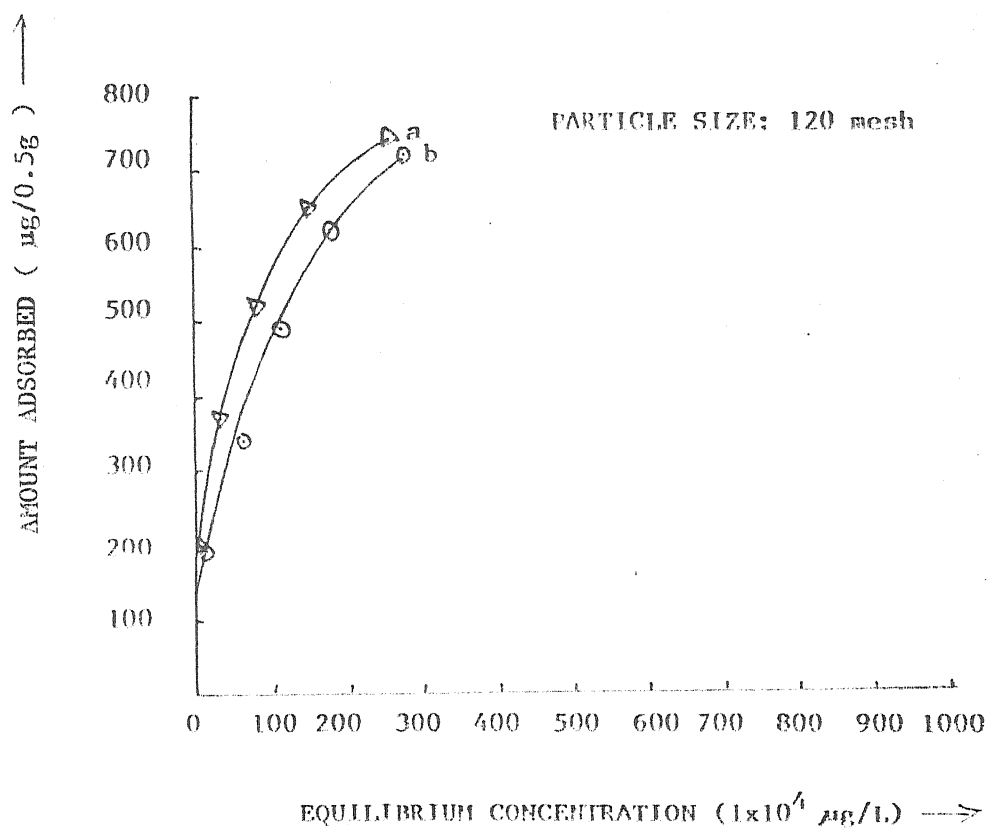


Fig.6: Adsorption isotherms for Methyl red on Unio Shell (a) 10 and (b) 25°

for its increasing initial concentrations. The partial molar free energy values were 392.32, 313.21, 215.51, 144.26 & 119.26 calories/mole respectively. The adsorptions at 25°C were 40.0, 35.0, 26.66, 20.0 & 16.0 percent and the respective values of partial molar free energy were 304.45, 256.74, 184.85, 132.99 & 103.91 calories/mole (Table 1 & 1a). In the increasing order of dye concentrations the curves showed an increase in the amount of adsorbate adsorbed by the adsorbent at both the temperatures (Fig.4).

The percent adsorptions (particle size:80 mesh) were 40.0, 32.5, 25.0, 18.75 & 15.0 at 10°C and the values obtained for partial molar free energy were 289.12, 222.46, 162.82, 117.52 & 91.98 calories/mole respectively. At 25°C the adsorptions were 30.0, 27.5, 21.66, 16.25 & 13.0 percent and the partial molar free energy values were 212.57, 191.66, 145.54, 105.69 & 83.0 calories/mole respectively (Table 2 & 2a). The curves showed similarity in nature as above (Fig. 10).

Methylene blue:

90.0, 75.0, 70.0, 63.75 & 57.0 percent Methylene blue was adsorbed on

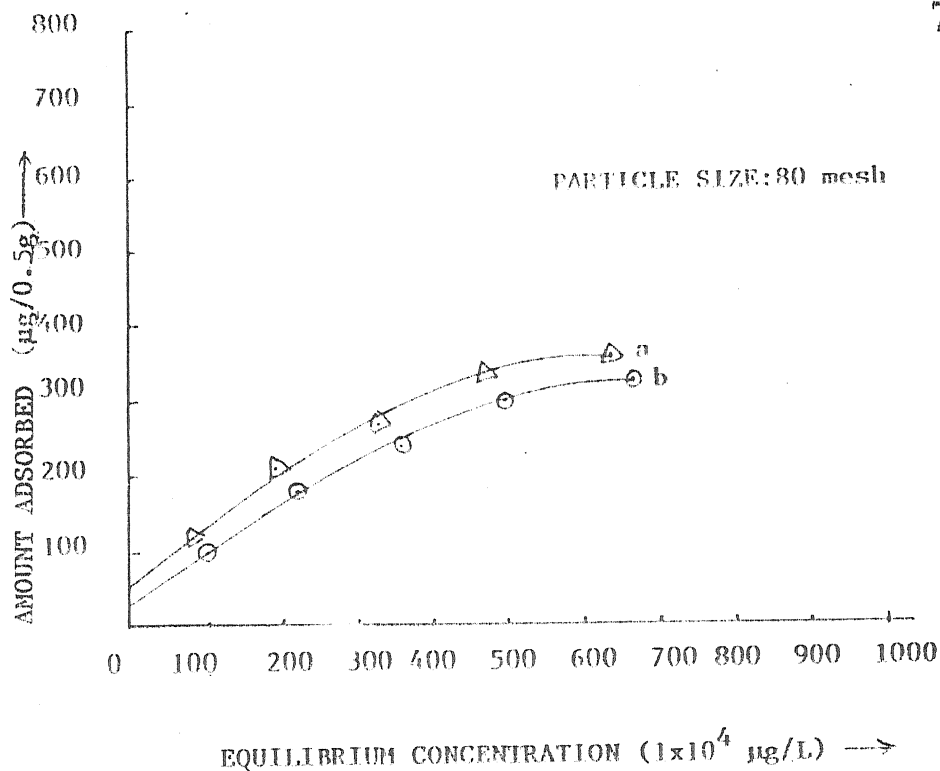
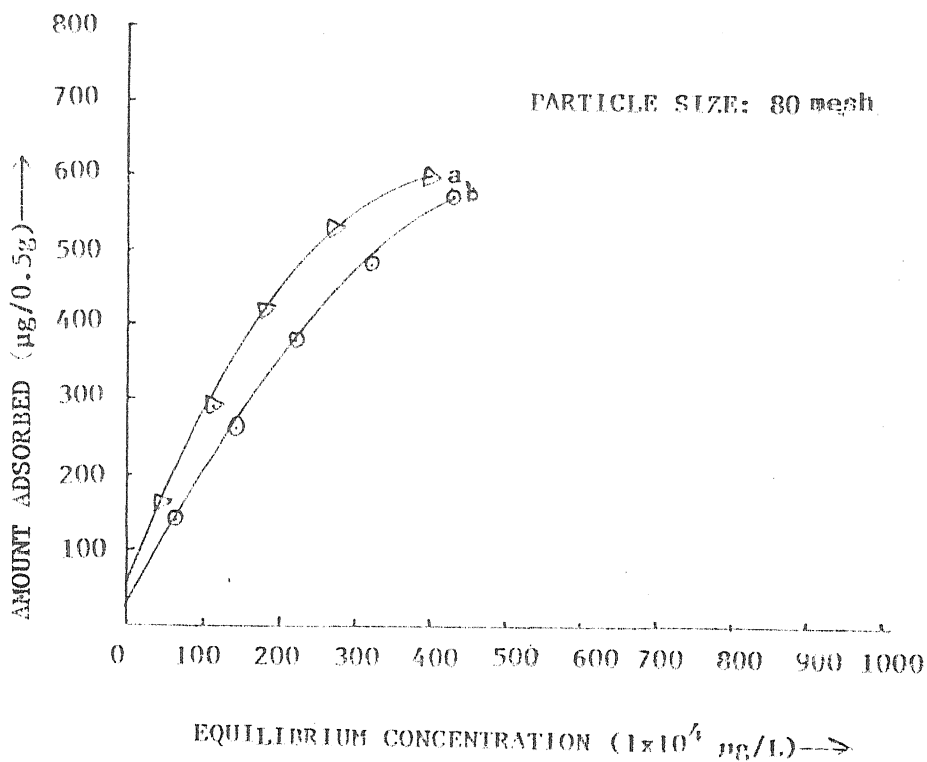


Fig.7: Adsorption Isotherms for Toluidine blue on Unio Shell (a) 10 and (b) 25"



Unio shells (particle size: 120 mesh) at 10°C and partial molar free energy values were 1303.26, 784.64, 681.44, 574.33 & 477.68 calories/mole respectively (Table 1 & 1a) for increasing initial concentrations of dye. The adsorptions at 25°C were 80.0, 67.5, 65.0, 61.25 & 52.0 percent and the corresponding values of partial molar free energy were 959.22, 669.86, 625.69, 563.03 & 437.44 calories/mole. At both the temperatures there was an increase in the amount of dye adsorbed on increasing the concentrations of the adsorbate, as shown by the curves (Fig. 5).

Experiments with the 80 mesh particle size of Unio shells showed 85.0, 72.5, 61.66, 57.5 & 50.0 percent adsorptions at 10°C. The partial molar free energy values were 1073.76, 730.69, 542.70, 484.30 & 392.32 calories/mole respectively. At 25°C the adsorptions were 75.0, 62.5, 58.33, 53.75 & 47.0 percent and the corresponding values of partial molar free energy were 826.23, 584.57, 521.77, 459.58 & 378.38 calories/mole (Table 2 & 2a). The nature of curves at 10°C and 25°C was similar as above (Fig. 11).

Methyl red:

At temperature 10°C the adsorptions of Methyl red on Unio

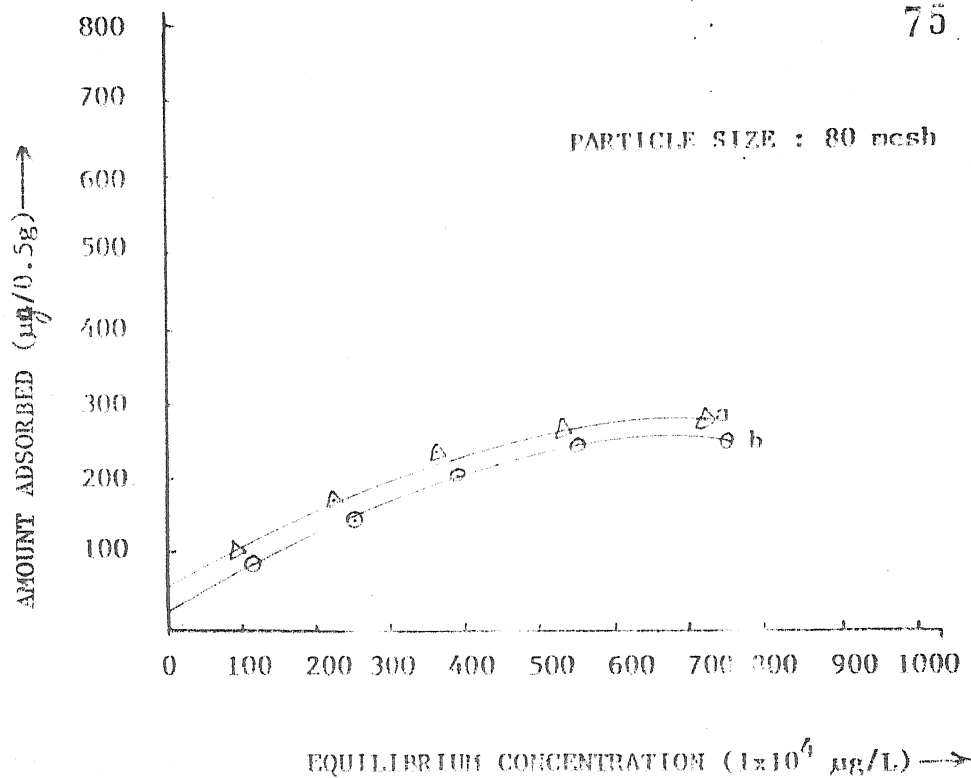
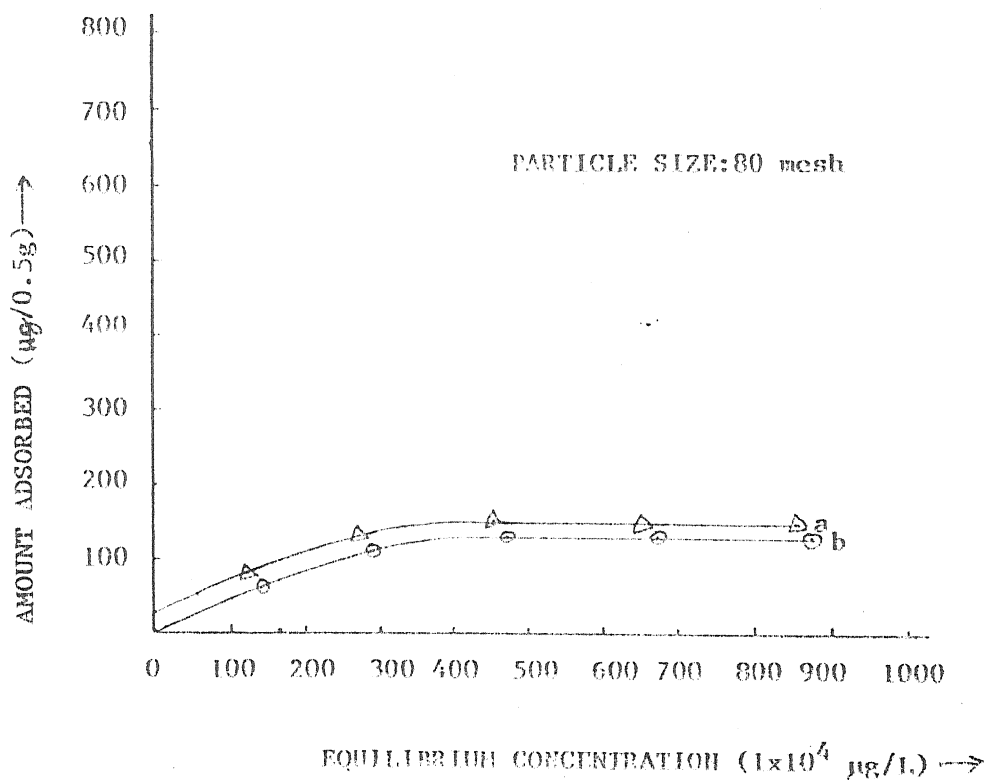


Fig. 9: Adsorption Isotherms for Trypsan blue on Unio Shell (a) 10 and (b) 25°



shells (particle size:120 mesh) were 100.0, 92.5, 86.66, 81.25 & 74.0 percent for increasing initial dye concentrations and the respective values of partial molar free energy were 3001.68, 1466.09, 1140.43, 947.47 & 762.44 calories/mole. At 25°C the order of adsorptions were 95.0, 85.0, 81.66, 77.5 & 72.0 percent and the corresponding values of partial molar free energy were 1785.45, 1130.68, 1011.08, 889.02 & 758.68 calories/mole (Table 1 & 1a). At both the temperatures the nature of curves showed an increase in the amount of adsorbate adsorbed on increasing the concentrations of dye (Fig. 6).

On 80 mesh particle size (Temperature :10°C), the adsorptions were 95.0, 85.0, 80.0, 75.0 & 72.0 percent and the calculated values of partial molar free energy were 1695.58, 1073.76, 910.94, 784.64 & 720.49 calories/mole respectively. The adsorptions at 25°C were 85.0, 80.0, 73.33, 71.25 & 68.0 percent and the respective values of partial molar free energy were 1130.68, 959.22, 787.76, 742.93 & 679.10 calories/mole (Table 2 & 2a). The curves at both the temperatures were of similar nature as above (Fig. 12).

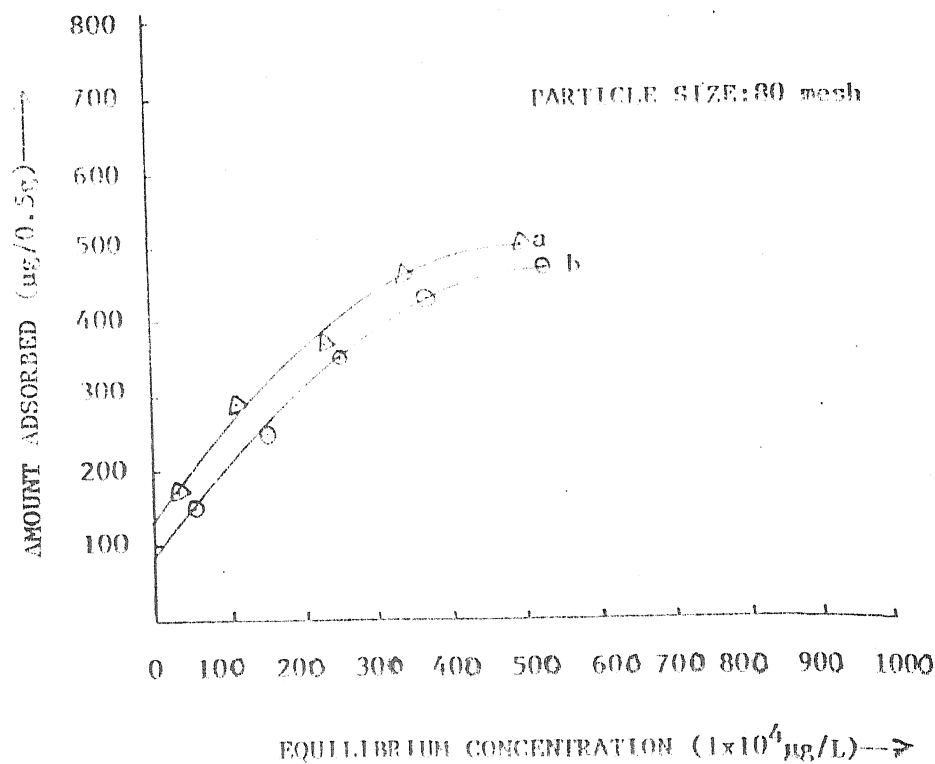
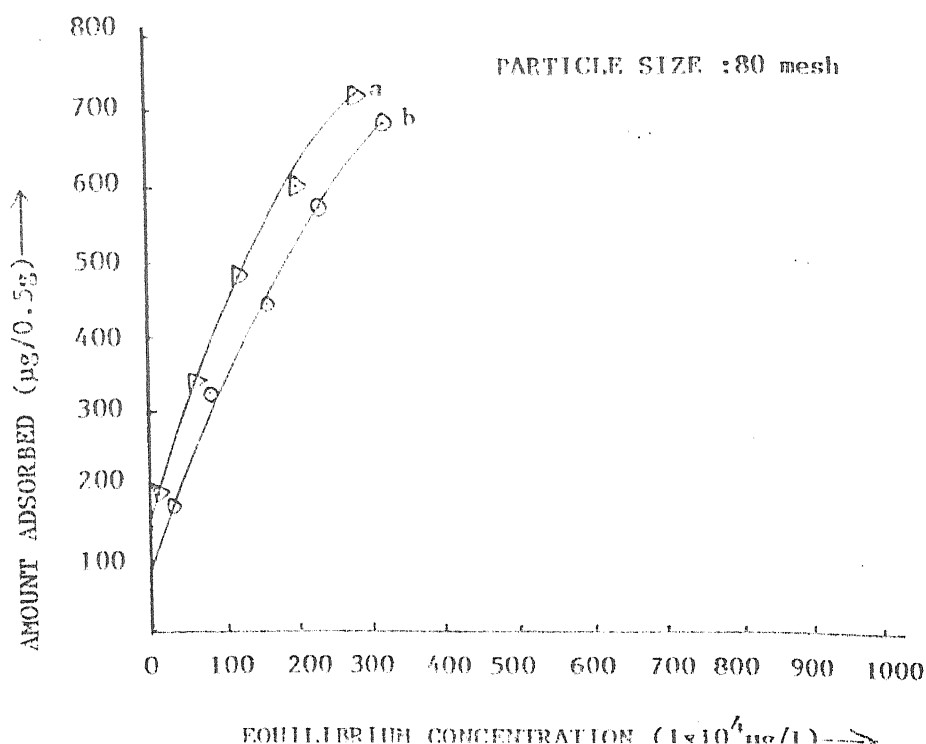


Fig.11: Adsorption Isotherms for Methylene blue on Unio Shell (a) 10 and (b) 25°



ADSORPTION OF DYES FROM EFFLUENTS ON UNIO SHELLS

Red coloured effluent:

The adsorptions on dye from red coloured effluent on Unio Shells (particle size : 120 mesh), at 10°C were 100.0, 92.5, 86.66, 80.0 & 74.0 percent, for 20.0, 40.0, 60.0, 80.0 & 100.0 percent initially concentrated solutions of the effluent respectively and the corresponding values of partial molar free energy were 3001.68, 1466.09, 1140.43, 910.94 & 762.44 calories/mole. At 25°C the percent adsorptions were 95.0, 87.5, 80.0, 76.25 & 70.0 and values of partial molar free energy were 1785.45, 1239.34, 959.22, 856.80 & 717.56 cal./mole respectively (Table 3 & 3a). The curves showed a steep rise in the amount of dye adsorbed on increasing the concentrations at both the temperatures (Fig. 13).

The adsorptions of Unio shells (particle size : 80 mesh) were 80.0, 80.0, 78.33, 75.0 & 70.0 percent at 10°C and partial molar free energy values were 910.94, 910.94, 865.63, 784.64 & 681.44 calories/mole respectively. The adsorptions at 25°C were 70.0, 70.0, 71.66, 68.75 & 66.0 percent and corresponding values of partial molar

Table - 3. Adsorption of dyes from effluents on Unio Shells
(particle size: 120 mesh)

Initial dye concentration (Percent)	Temperature 10° C		Temperature 25° C	
	Equilibrium	Amount of	Equilibrium	Amount of
	dye concent-	dye	dye concent-	dye
	ration	adsorbed	ration	adsorbed
	(Percent)	(Percent/0.5g)	(Percent)	(Percent/0.5g)

Red coloured effluent:

20	0	20	1	19
40	3	37	5	35
60	8	52	12	48
80	16	64	19	61
100	26	74	30	70

Violet coloured effluent:

20	3	17	7	13
40	14	26	18	22
60	25	35	29	31
80	38	42	44	36
100	57	43	62	38

Sky blue coloured effluent:

20	9	11	12	8
40	21	19	24	16
60	34	26	38	22
80	49	31	52	28
100	65	35	69	31

Continuation of Table - 3.

Yellow coloured effluent:

20		9		11		12		8
40		21		19		26		14
60		36		24		39		21
80		50		30		54		26
100		68		32		72		28

Green coloured effluent:

20		0		20		2		18
40		8		32		10		30
60		17		43		20		40
80		29		51		32		48
100		44		56		48		52

Orange coloured effluent:

20		1		19		3		17
40		7		33		9		31
60		15		45		17		43
80		24		56		27		53
100		36		64		40		60

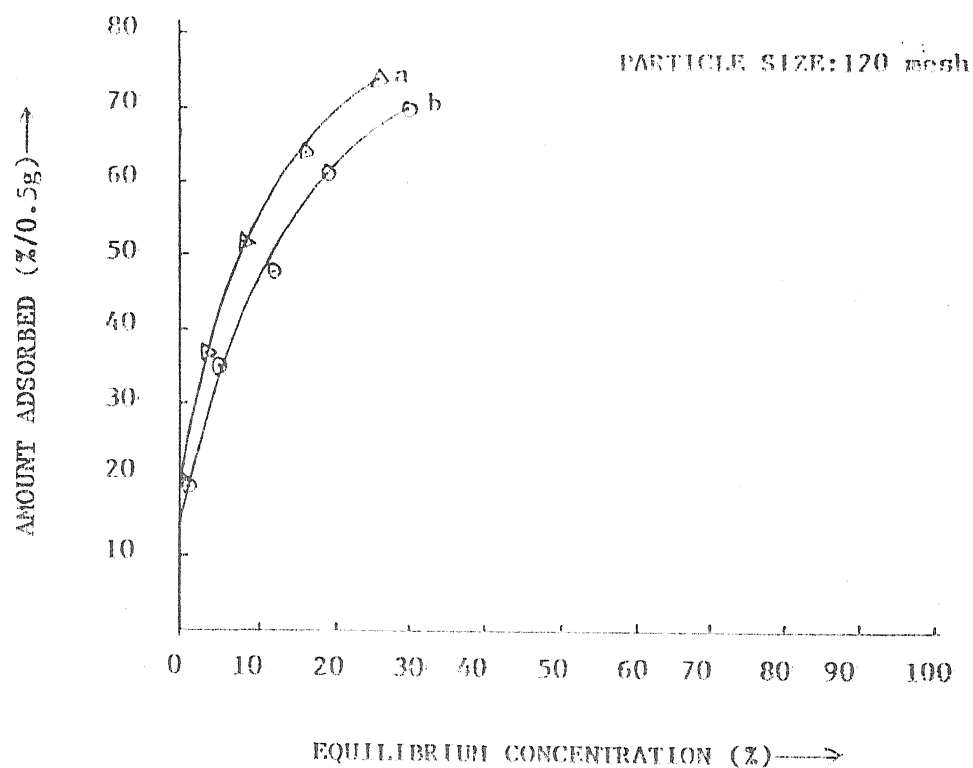


Fig.13: Adsorption Isotherms for Red coloured effluent on Unio Shell (a) 10 and (b) 25°

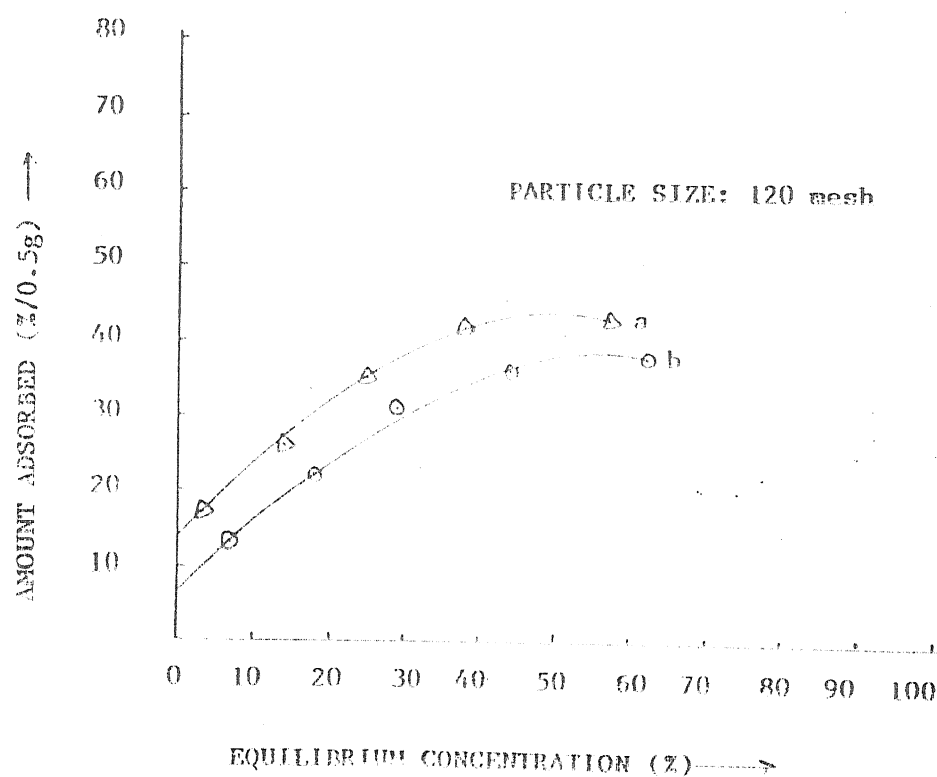


Fig.14: Adsorption Isotherms for Violet Coloured effluent on Unio Shell (a) 10 and (b) 25°

free energy were 717.56, 717.56, 751.63, 693.23 & 642.97 calories/mole (Table 4 & 4a). The curves showed similarity with the above mentioned curves in their nature at both the temperatures (Fig.19).

Violet coloured effluent:

On particle size 120 mesh of Unio shells the dye from violet coloured effluent adsorbed were 85.0, 65.0, 58.33, 52.5 & 43.0 percent for 20.0, 40.0, 60.0, 80.0 & 100.0 percent initially concentrated effluent respectively at 10°C. The corresponding partial molar free energy values were 1073.76, 594.19, 495.51, 421.35 & 318.15 calories/mole. The adsorptions at 25°C were 65.0, 55.0, 51.66, 45.0 & 38.0 percent and the respective values of partial molar free energy were 625.69, 475.91, 433.32, 356.31 & 284.90 calories/mole (Table 3 & 3a). At both the temperatures the curves showed an increase in the amount of dye from effluent adsorbed, on increasing the concentrations (Fig.14).

On particle size 80 mesh of Unio shells (temperature:10°C) the adsorptions were 60.0, 52.5, 51.66, 48.75 & 41.0 percent and the respective values of partial molar free energy were 518.62,

Table 3 a: Adsorption of dyes from effluents on Unio Shells
(Particle size : 120 mesh)

Initial dye concentration (Percent)	TEMPERATURE 10°C		TEMPERATURE 25°C	
	Percent	Partial molar	Percent	Partial molar
	adsorption	free energy	adsorption	free energy
		$-\bar{G}$ (Cals./Mole)		$-\bar{G}$ (Cals./Mole)

Red coloured effluent:

20	100.00	3001.68	95.00	1785.45
40	92.5	1466.09	87.5	1239.34
60	86.66	1140.43	80.0	959.22
80	80.0	910.94	76.25	856.80
100	74.0	762.44	70.0	717.56

Violet coloured effluent:

20	85.0	1073.76	65.0	625.69
40	65.0	594.19	55.0	475.91
60	58.33	495.51	51.66	433.32
80	52.50	421.35	45.0	356.31
100	43.0	318.15	38.0	284.90

Sky blue coloured effluent:

20	55.0	451.95	40.0	304.45
40	47.5	364.70	40.0	304.45
60	43.33	321.47	36.66	272.22
80	38.75	277.45	35.0	256.74
100	35.0	243.82	31.0	221.15

Continuation of table 3 a:

Yellow coloured effluent:

20		55.00		451.95		40.00		304.45
40		47.50		364.70		35.00		256.74
60		40.00		289.12		35.00		256.74
80		37.50		266.02		32.50		234.25
100		32.00		218.28		28.00		195.78

Green coloured effluent:

20		100.00		3001.68		90.00		1372.34
40		80.00		910.94		75.00		826.23
60		71.66		713.80		66.66		654.77
80		63.75		574.33		60.00		546.10
100		56.00		464.67		52.00		437.44

Orange coloured effluent:

20		95.00		1695.58		85.00		1130.68
40		82.50		986.52		77.50		889.02
60		75.00		784.64		71.66		751.63
80		70.00		681.44		66.25		647.36
00		64.00		578.25		60.00		546.10

421.35, 411.50, 378.34 & 298.64 calories/mole. At 25°C the adsorptions were 50.0, 50.0, 48.33; 46.25 & 38.0 percent and respective values of partial molar free energy were 413.11, 413.11, 393.57, 370.01 & 284.90 calories/mole (Table 4 & 4a). At both the temperatures the amount of dye from effluent adsorbed increased at the increase of concentrations (Fig. 20).

Sky blue coloured effluent:

20.0, 40.0, 60.0, 80.0 & 100.0 percent initially concentrated solutions of dye from sky blue coloured effluent were adsorbed on Unio shells (Particle size: 120 mesh) to the extent of 55.0, 47.5, 43.33, 38.75 & 35.0 percent respectively at 10°C and the respective values of partial molar free energy were 451.95, 364.70, 321.47, 277.45 & 243.82 calories/mole. The adsorptions at 25°C were 40.0, 40.0, 36.66, 35.0 & 31.0 percent and the respective values of partial molar free energy were 304.45, 304.45, 272.22, 256.74 & 221.15 calories/mole (Table 3 & 3a). On increasing the concentrations the amount of adsorbate adsorbed on Unio shells at both the temperatures was increased as shown in the curves (Fig. 15).

On 80 mesh particle size (Temperature: 10°C) the

Table - 4. Adsorption of dyes from effluents on Unio Shells
(particle size: 80 mesh)

Initial dye concentration (Percent)	Temperature 10° C		Temperature 25° C	
	Equilibrium dye concent- ration (Percent)	Amount of dye adsorbed (Percent/0.5g)	Equilibrium dye concent- ration (Percent)	Amount of dye adsorbed (Percent/0.5g)

Red coloured effluent:

20	4	16	6	14
40	8	32	12	28
60	13	47	17	43
80	20	60	25	55
100	30	70	34	66

Violet coloured effluent:

20	8	12	10	10
40	19	21	20	20
60	29	31	31	29
80	41	39	43	37
100	59	41	62	38

Sky blue coloured effluent:

20	12	8	13	7
40	25	15	27	13
60	39	21	41	19
80	53	27	55	25
100	68	32	72	28

Contd.....

Continuation of Table - 4.

Yellow coloured effluent:

20		12		8		13		7
40		25		15		27		13
60		40		20		42		18
80		53		27		57		23
100		71		29		75		25

Green Coloured effluent:

20		6		14		8		12
40		14		26		16		24
60		23		37		26		34
80		34		46		37		43
100		48		52		51		49

Orange coloured effluent:

20		3		17		5		15
40		9		31		11		29
60		17		43		20		40
80		28		52		31		49
100		41		59		45		55

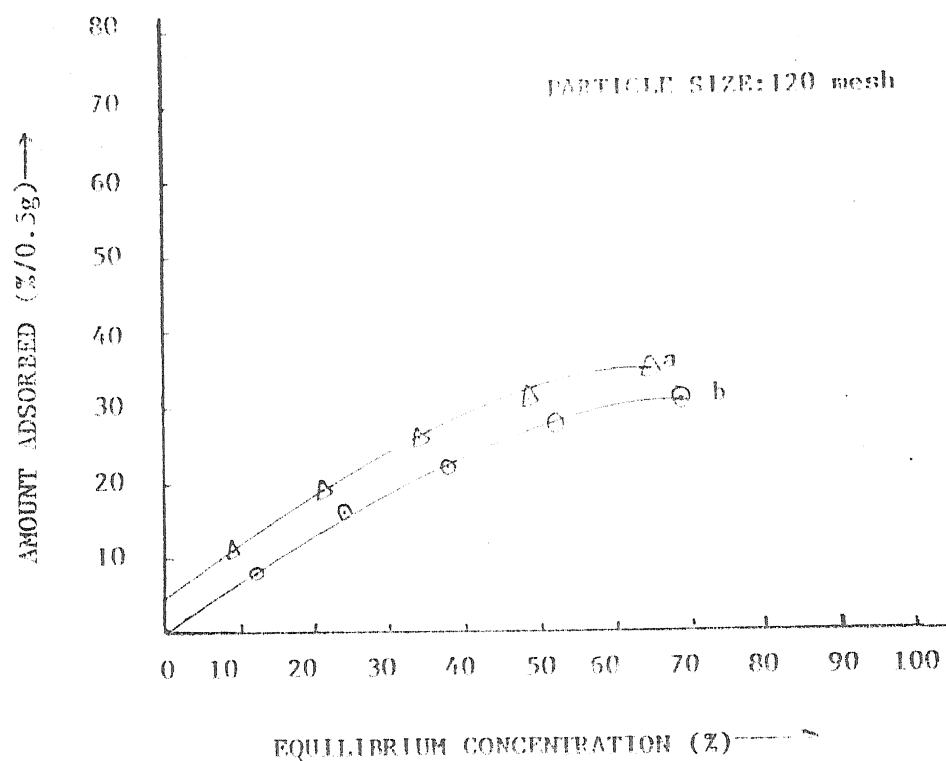


Fig.15: Adsorption Isotherms for Sky blue coloured effluent on Unio Shell (a) 10 and (b) 25°

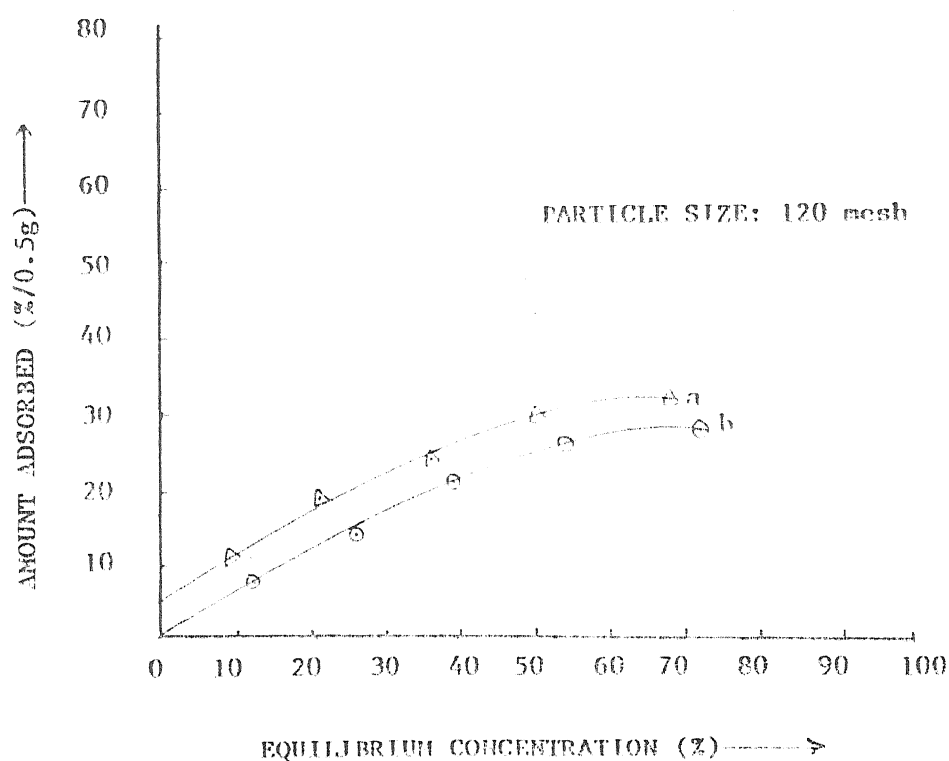


Fig.16: Adsorption isotherms for Yellow coloured effluent on Unio Shell (a) 10 and (b) 25°

adsorptions were 40.0, 37.5, 35.0, 33.75 & 32.0 percent and the corresponding values of partial molar free energy were 289.12, 266.02, 243.82, 233.04 & 218.28 calories/mole. The adsorptions were 35.0, 32.5, 31.66, 31.25 & 28.0 percent at 25°C and the partial molar free energy values were 256.74, 234.25, 226.94, 223.31 & 195.78 calories/mole respectively (Table 4 & 4a). There was a similarity in the nature of curves with the above curves at both the temperatures (Fig. 21).

Yellow coloured effluent:

The adsorptions of dye from yellow coloured effluent on Unio shells (particle size: 120 mesh) were 55.0, 47.5, 40.0, 37.5, & 32.0 percent respectively for 20.0, 40.0, 60.0, 80.0 & 100.0 percent initially concentrated effluent at 10°C and the corresponding values of partial molar free energy were 451.95, 364.70, 289.12, 266.02 & 218.28 calories/mole. The adsorptions of this dye on Unio shells were 40.0, 35.0, 35.0, 32.5 & 28.0 percent at 25°C and the corresponding values of partial molar free energy were 304.45, 256.74, 256.74, 234.25 & 195.78 calories/mole (Table 3 & 3a). The curves at both the temperatures showed an increase in the amount of dye adsorbed on increase of concentrations of dye in the effluent (Fig.16).

Table 4 a: Adsorption of dyes from effluents on Unio Shells
(Particle size : 80 mesh)

Initial dye	TEMPERATURE 10°C		TEMPERATURE 25°C	
concentration	Percent	Partial Molar	Percent	Partial molar
(Percent)	adsorption	free energy	adsorption	free energy
		$-\bar{G}(\text{Cals./Mole})$		$-\bar{G}(\text{Cals./Mole})$

Red coloured effluent:

20	80.0	910.94	70.0	717.56
40	80.0	910.94	70.0	717.56
60	78.33	865.63	71.66	751.63
80	75.0	784.64	68.75	693.23
100	70.0	681.44	66.0	642.97

Violet coloured effluent:

20	60.0	518.62	50.0	413.11
40	52.5	421.35	50.0	413.11
60	51.66	411.50	48.33	393.57
80	48.75	378.34	46.25	370.01
100	41.00	298.64	38.0	284.90

Sky blue coloured effluent:

20	40.0	289.12	35.0	256.74
40	37.5	266.02	32.5	234.25
60	35.00	243.82	31.66	226.94
80	33.75	233.04	31.25	223.31
100	32.0	218.28	28.0	195.78

Continuation of table 4 a:

Yellow coloured effluent:

20		40.0		289.12		35.0		256.74
40		37.5		266.02		32.5		234.25
60		33.33		229.49		30.0		212.57
80		33.75		233.04		28.75		202.02
100		29.0		193.84		25.0		171.45

Green coloured effluent:

20		70.0		681.44		60.0		546.10
40		65.0		594.19		60.0		546.10
60		61.66		542.70		56.66		498.40
80		57.5		484.30		53.75		459.58
100		52.00		415.42		49.0		401.31

Orange coloured effluent:

20		85.0		1073.76		75.0		826.23
40		77.5		844.27		72.5		769.42
60		71.66		713.80		66.66		654.77
80		65.0		594.19		61.25		565.03
100		59.0		504.64		55.0		475.91

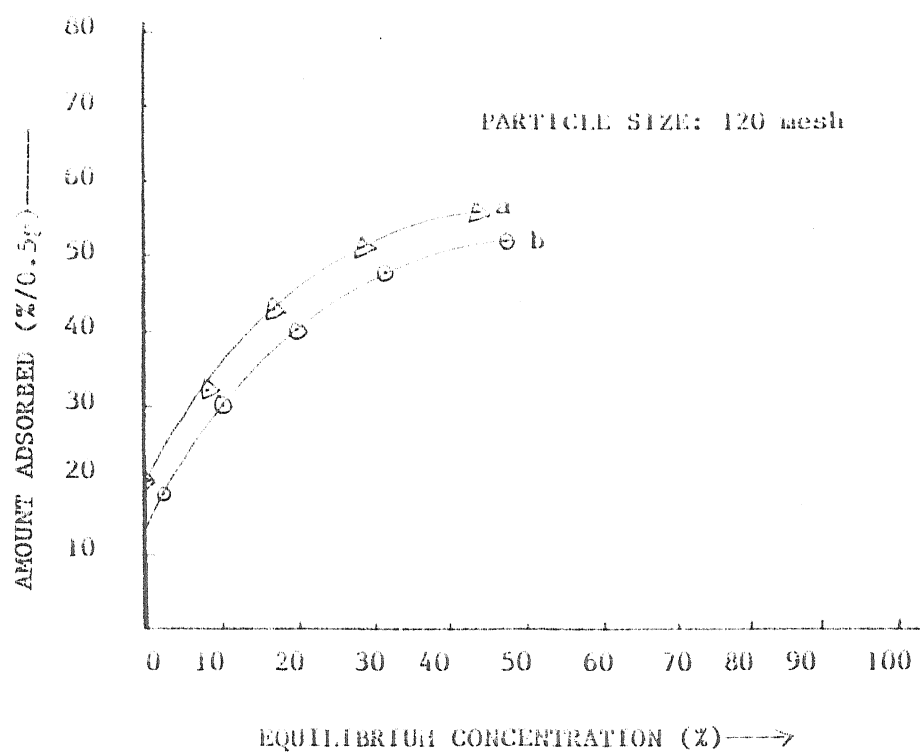


Fig.17: Adsorption isothermas for Green coloured effluent on Unio Shell (a) 10 and (b) 25°

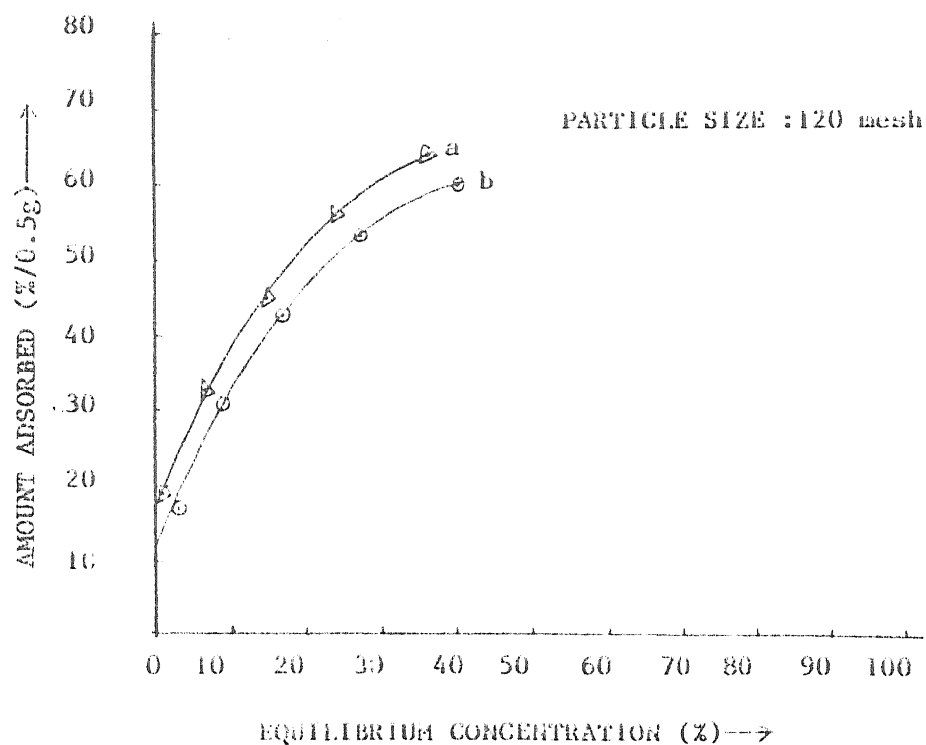


Fig.18: Adsorption isothermas for Orange coloured effluent on Unio Shell (a) 10 and (b) 25°

The experiments on 80 mesh particle size showed that 40.0, 37.5, 33.33, 33.75 & 29.0 percent dye from effluent were adsorbed at 10°C and partial molar free energy values were 289.12, 266.02, 229.49, 233.04 & 193.84 calories/mole respectively. At 25°C the adsorptions were 35.0, 32.5, 30.0, 28.75 & 25.0 percent and the respective values of partial molar free energy were 256.74, 234.25, 212.57, 202.02 & 171.45 calories/mole (Table 4 & 4a). The nature of curves was similar to the above mentioned curves at 10°C and 25°C (Fig. 22).

Green coloured effluent:

The order of percent adsorptions of the dye from Green coloured effluent on *Unio* shells (particle size: 120 mesh) at 10°C were 100.0, 80.0, 71.66, 63.75 & 56.0 respectively for 20.0, 40.0, 60.0, 80.0 & 100.0 percent initially dye concentrated effluent solution and the respective values of partial molar free energy were 3001.68, 910.94, 713.80, 574.33 & 464.67 calories/mole (Table 3 & 3a). On increasing the concentrations of dye the curves showed an increase in the amount of dye adsorbed at both the temperatures (Fig. 17).

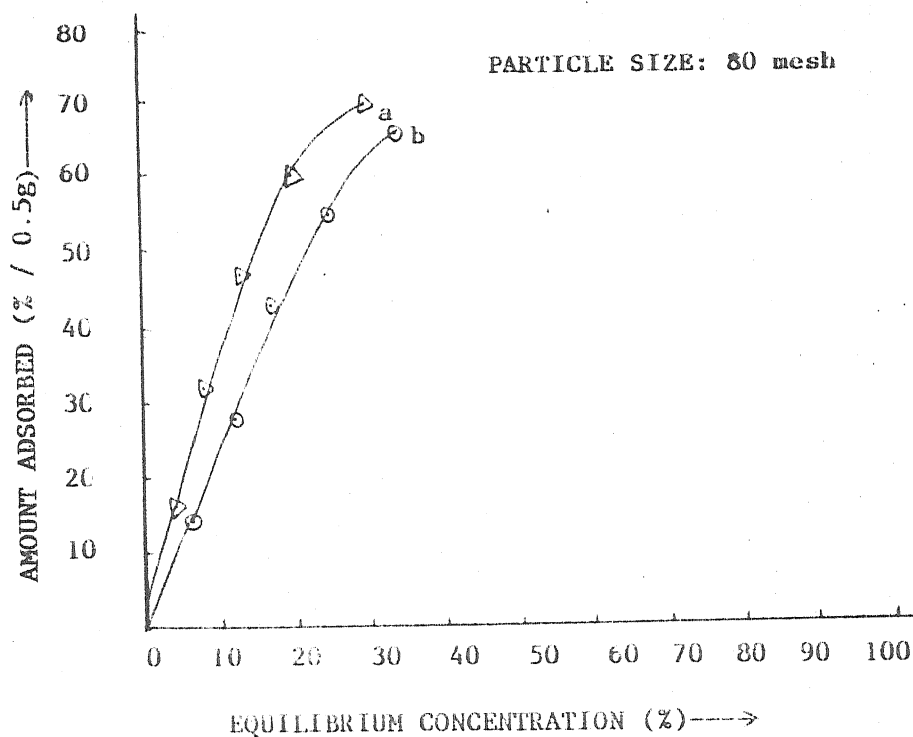


Fig.19: Adsorption Isotherms for Red coloured effluent on Unio Shell (a) 10 and (b) 25°

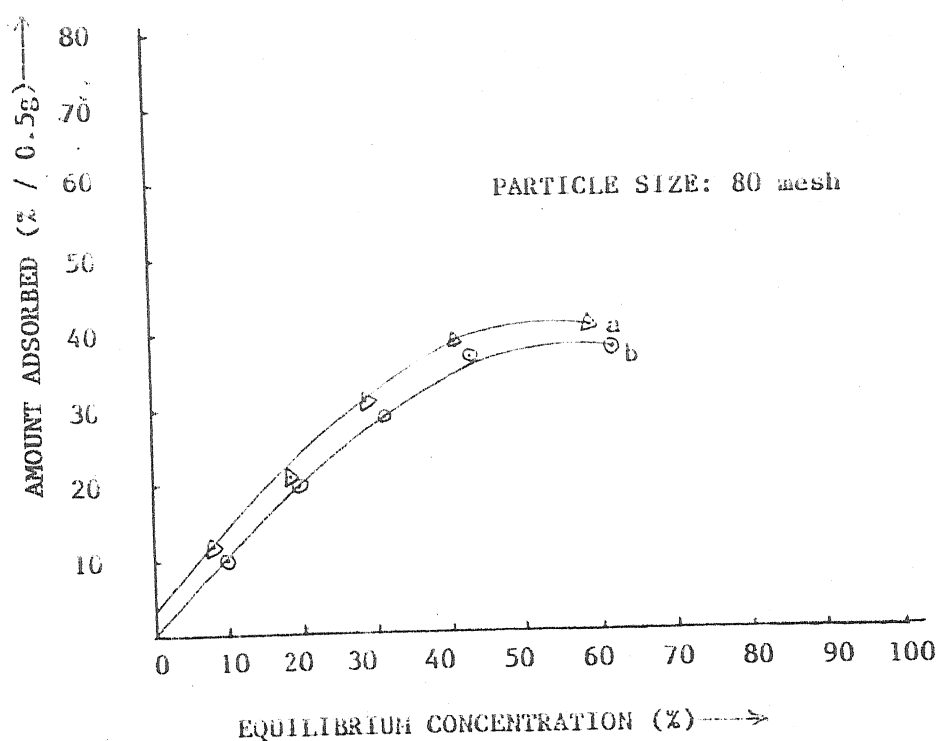


Fig.20: Adsorption Isotherms for Violet coloured effluent on Unio Shell (a) 10 and (b) 25°

On 80 mesh particle size of Unio shells (Temperature:10°C) the percent adsorptions were 70.0, 65.0, 61.66, 57.0 & 52.0 respectively and the corresponding values of partial molar free energy were 681.44, 594.19, 542.70, 484.30 & 415.42 calories/mole. At 25°C the adsorptions were 60.0, 60.0, 56.66, 53.75 & 49.0 percent respectively and the respective values of partial molar free energy were 546.10, 546.10, 498.40, 459.58 & 401.31 calories/mole (Table 4 & 4a). The curves were similar in nature as above at both the temperatures (Fig. 23).

Orange coloured effluent:

At temperature 10°C, dye from effluent adsorbed were 95.0, 82.5, 75.0, 70.0 & 64.0 percent respectively out of 20.0, 40.0, 60.0, 80.0 & 100.0 percent initially dye concentrated, on Unio shells (particle size: 120 mesh) and the corresponding values of partial molar free energy were 1695.58, 986.52, 784.64, 681.44 & 578.25 calories/mole. At 25°C amounts of adsorbate absorbed were 85.0, 77.5, 71.66, 66.25 & 60.0 percent and respective values of partial molar free energy were 1130.68, 889.02, 751.63, 647.36 & 546.10 calories/mole (Table 3 & 3a).

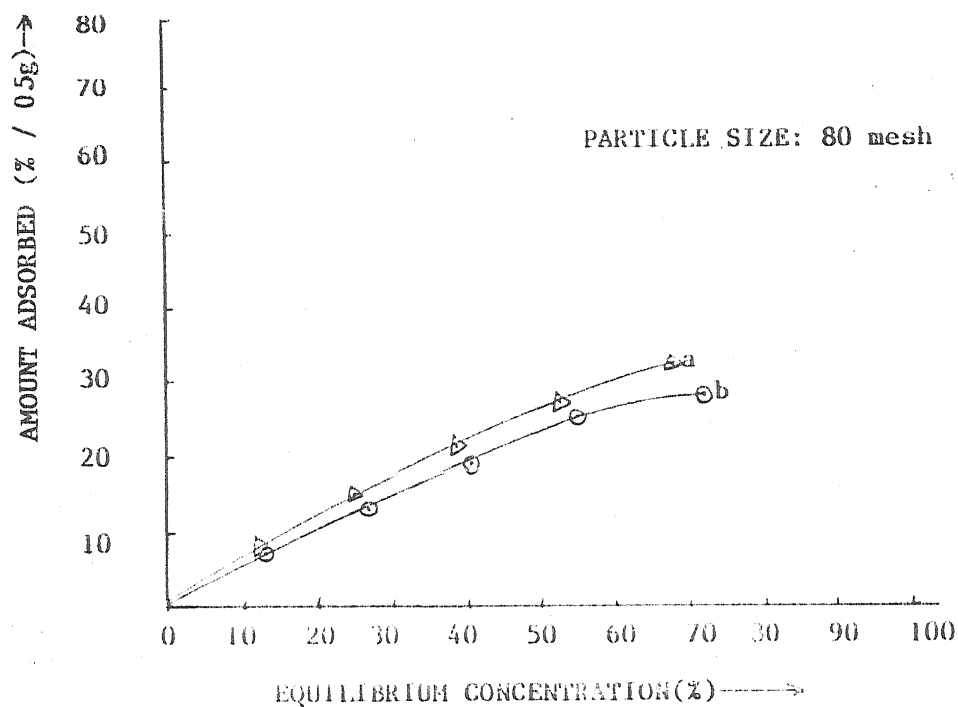


Fig. 21: Adsorption Isotherms for Sky blue coloured effluent on Unio Shell (a) 10 and (b) 25°

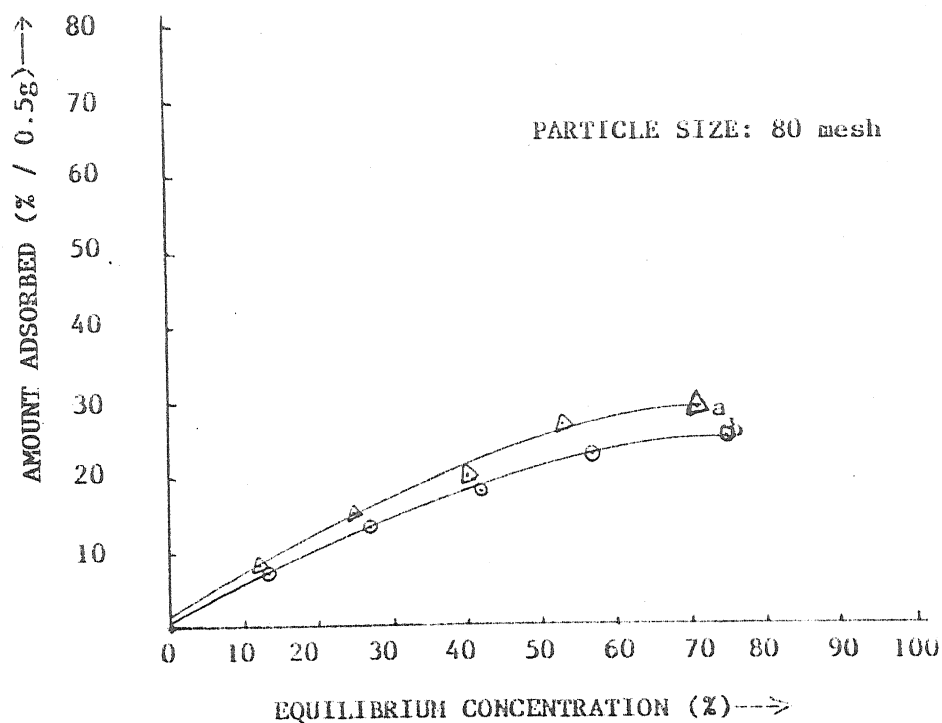


Fig. 22: Adsorption Isotherms for Yellow coloured effluent on Unio Shell (a) 10 and (b) 25°

For the above study the curves plotted for amounts of dye adsorbed against equilibrium concentrations revealed an increase in the amount of adsorbate adsorbed, on increase of dye's concentrations (Fig. 18).

On 80 mesh particle size, 85.0, 77.5, 71.66, 65.0 & 59.0 percent dye from effluent was adsorbed respectively for increasing order of initial dye concentration at 10°C . The respective values of partial molar free energy were 1073.76, 844.27, 713.80, 594.19 & 504.64 calories/mole. Adsorptions at 25°C were 75.0, 72.5, 66.66, 61.25 & 55.0 percent respectively and the respective values of partial molar free energy were 826.23, 769.42, 654.77, 565.03 & 475.91 calories/mole. At temperature 10°C and 25°C , curves were of similar in nature as above (Fig. 24).

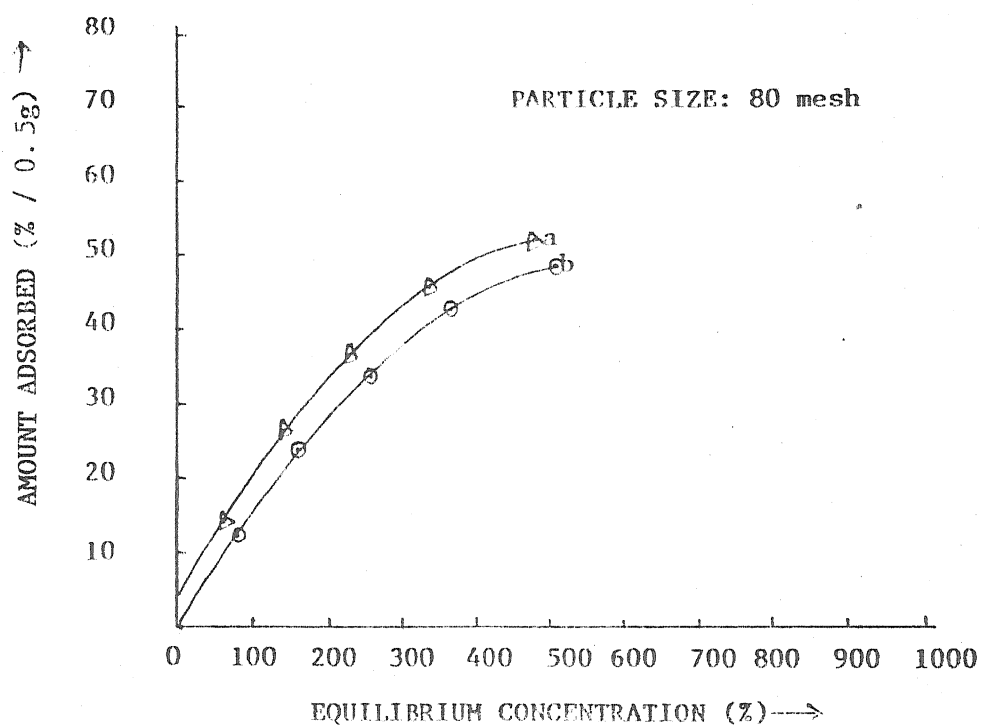


Fig.23: Adsorption Isotherms for Green coloured effluent on Unio Shell (a) 10 and (b) 25°

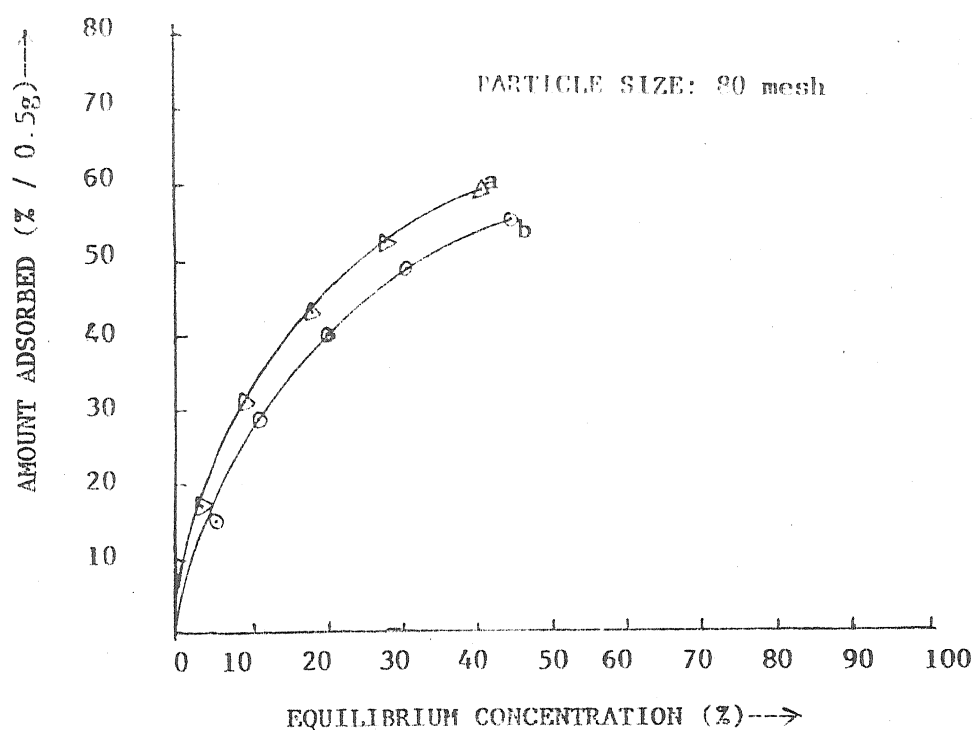


Fig.24: Adsorption Isotherms for Orange coloured effluent on Unio (a) 10 and (b) 25°

ADSORPTION OF DYES ON PIIA SHELLS

Toluidine blue:

On 120 mesh particle size of Pila shells, the adsorptions of Toluidine blue were 90.0, 72.5, 68.33, 63.75 & 55.0 percent respectively for increasing order of initial dye concentrations at 10°C and the respective values of partial molar free energy were 1303.26, 730.69, 650.84, 574.33 & 451.95 calories/mole. The percent adsorptions of Toluidine blue at 25°C were 75.0, 62.5, 63.33, 57.5 & 50.0 for the above said order of initial dye concentrations and the respective values of partial molar free energy were 826.23, 584.57, 597.96, 509.97 & 413.11 calories/mole (Table 5 & 5a). The curves showed an steep rise initially and then comparatively slow increase in the amount of dye adsorbed on increasing the concentrations (Fig. 25) at both the temperatures.

On Pila shells (particle size:80 mesh) the adsorptions of Toluidine blue were 80.0, 65.0, 58.33, 52.5 & 47.0 percent for gradually increase of initial dye concentrations at 10°C and the calculated values of partial molar free energy were 910.94, 594.19, 495.51, 421.35 & 359.34 calories/mole respectively. At 25°C, 65.0,

Table - 5. Adsorption of dyes on Pila Shells (Particle size: 120 Mesh)

Initial dye concentration ($1 \times 10^4 \mu\text{g/L}$)	Temperature 10°C		Temperature 25°C	
	Equilibrium	Amount of	Equilibrium	Amount of
	dye concent-	dye	dye concent-	dye
	ration ($1 \times 10^4 \mu\text{g/L}$)	adsorbed ($\mu\text{g}/0.5\text{g}$)	ration ($1 \times 10^4 \mu\text{g/L}$)	adsorbed ($\mu\text{g}/0.5\text{g}$)
Toluidine blue:				
200	20	180	50	150
400	110	290	150	250
600	190	410	220	380
800	290	510	340	460
1000	450	550	500	500
Crystal violet:				
200	00	200	00	200
400	20	380	40	360
600	30	570	60	540
800	60	740	100	700
1000	130	870	150	850
Trypsan blue:				
200	30	170	60	140
400	140	260	170	230
600	250	350	280	320
800	390	410	420	380
1000	550	450	580	420

Contd.....

Continuation of Table - 5.

Rhodamine B:

200		60		140		80		120
400		210		190		230		170
600		380		220		420		180
800		590		210		610		190
1000		770		230		810		190

Methylene blue:

200		00		200		00		200
400		20		380		40		360
600		40		560		60		540
800		100		700		160		640
1000		240		760		310		690

Methyl red:

200		00		200		00		200
400		20		380		40		360
600		50		550		70		530
800		90		710		110		690
1000		180		820		200		800

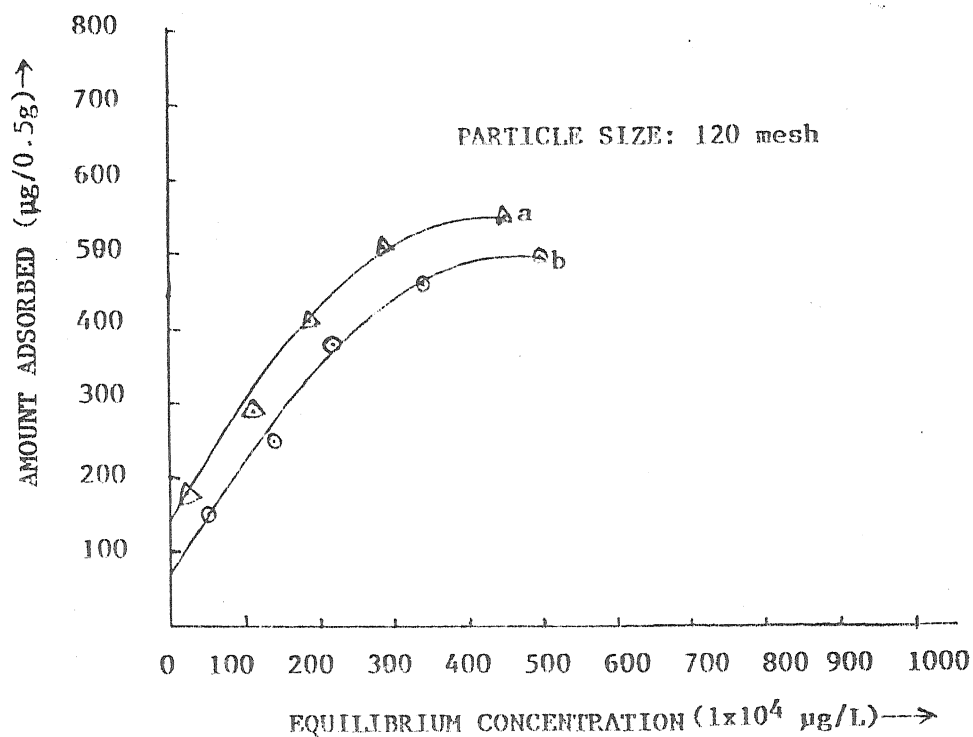


Fig.25:Adsorption Isotherms for Toluidine Blue on Pila Shell (a) 10 and (b) 25°

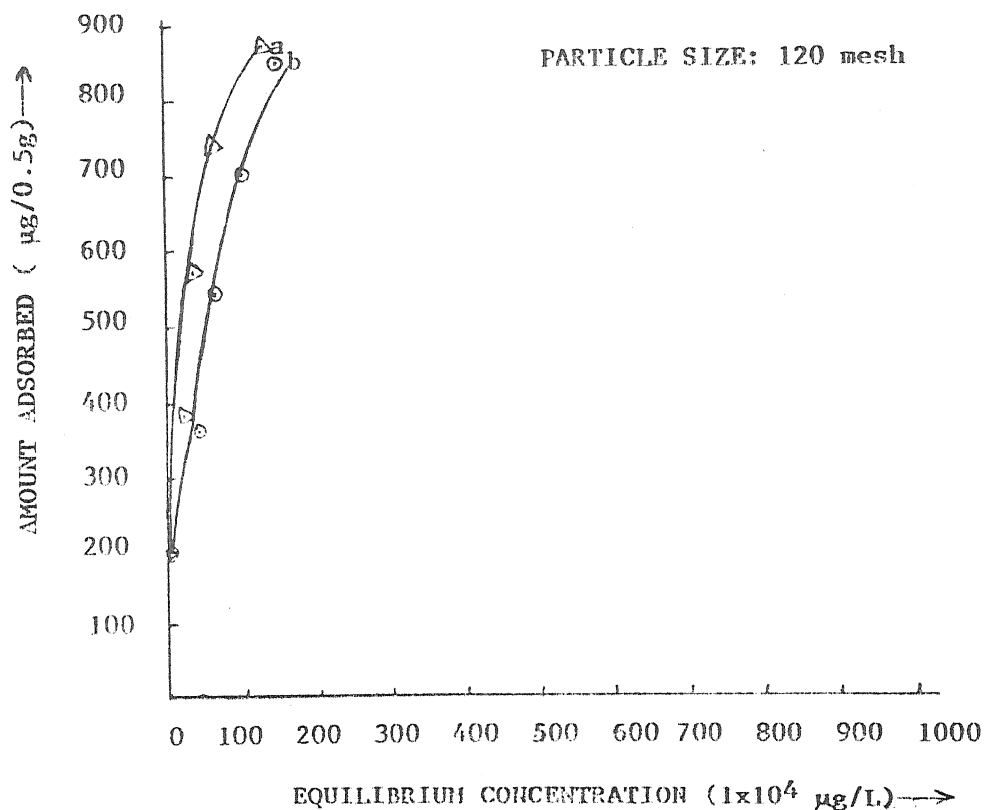


Fig.26:Adsorption Isotherms for Crystal violet on Pila Shell(a) 10 and(b) 25°

50.0, 50.0, 46.25 & 43.0 percent Toluidine blue was adsorbed respectively and 625.69, 413.11, 413.11, 370.01 & 335.02 calories/mole values of partial molar free energy were obtained (Table 6 & 6a). At both the temperatures the curves showed an increase in the amount of adsorbate adsorbed on increasing the concentrations (Fig. 31).

Crystal violet:

The adsorptions of Crystal violet at 10°C on Pila shells (Particle size: 120 mesh) were 100.0, 95.0, 95.0, 92.5 & 87.0 percent for its increasing initial concentrations and the values of partial molar free energy were 3001.68, 1695.58, 1695.58, 1466.09 & 1154.76 calories/mole respectively. The order of percent adsorptions at 25°C were 100.0, 90.0, 90.0, 87.5 & 85.0 and the respective partial molar free energy values were 3160.78, 1372.34, 1372.34, 1239.34 & 1130.68 calories/mole (Table 5 & 5a). The curves at both the temperatures showed a marked increase in the amount of dye adsorbed on increase of its concentrations (Fig. 26).

For increasing order of initial concentrations at 10°C, the adsorptions were 95.0, 90.0, 90.0, 87.5 & 84.0 percent on 80 mesh

Table 5 a. Adsorption of dyes on Pila Shells (Particle size: 120 Mesh)

Initial dye concentration (1×10^4 ug/L.)	TEMPERATURE 10°C		TEMPERATURE 25°C	
	Percent adsorption	Partial molar free energy $-\bar{G}$ (Cals/Mole)	Percent adsorption	Partial molar free energy $-\bar{G}$ (Cals/Mole)

Toluidine blue:

200	90.0	1303.26	75.0	826.23
400	72.5	730.69	62.5	584.57
600	68.33	650.84	63.33	597.96
800	63.75	574.33	57.50	509.97
1000	55.0	451.95	50.0	413.11

Crystal violet:

200	100.0	3001.68	100.0	3160.78
400	95.0	1695.58	90.0	1372.34
600	95.0	1695.58	90.0	1372.34
800	92.5	1466.09	87.5	1239.34
1000	87.0	1154.76	85.0	1130.68

Trypsan blue:

200	85.0	1073.76	70.0	717.56
400	65.0	594.19	57.5	509.97
600	58.33	495.51	53.33	454.23
800	51.25	406.65	47.5	384.03
1000	45.0	338.37	42.0	324.65

Continuation of table 5 a.

Rhodamine B:

200		70.0		681.44		60.0		546.10
400		47.5		364.70		42.5		329.81
600		36.66		258.52		30.0		212.57
800		26.25		172.34		23.75		161.60
1000		23.0		147.93		19.0		125.58

Methylene blue:

200		100.0		3001.68		100.0		3160.78
400		95.0		1695.58		90.0		1372.34
600		93.33		1532.75		90.0		1372.34
800		87.50		1176.96		80.0		959.22
1000		76.0		807.74		69.0		698.02

Methyl red:

200		100.0		3001.68		100.0		3160.78
400		95.0		1695.58		90.0		1372.34
600		91.66		1406.45		88.33		1280.46
800		88.75		1236.59		86.25		1182.54
1000		82.0		970.57		80.0		959.22

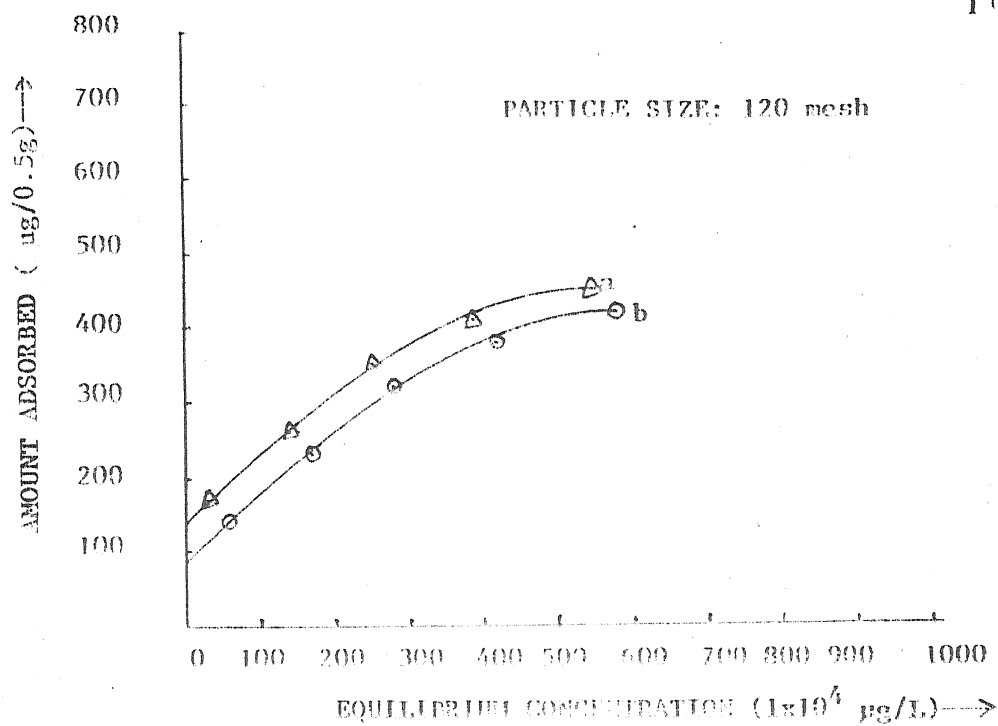


Fig. 27: Adsorption Isotherms for Trypan blue on Pils Shell (a) 10 and (b) 25°

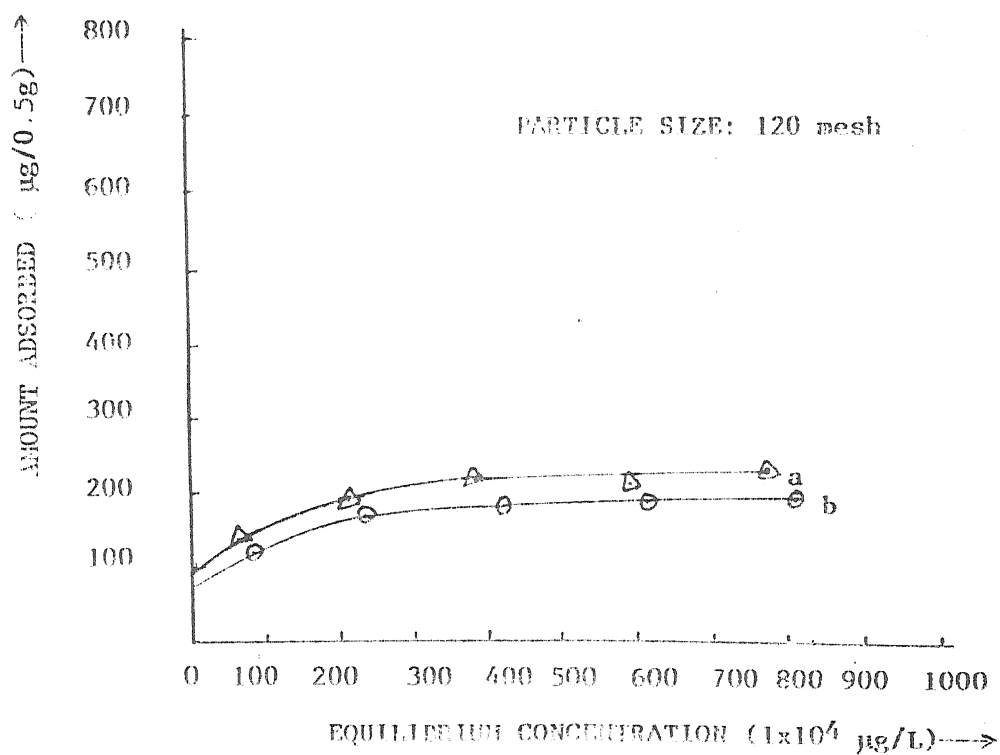


Fig. 28: Adsorption Isotherms for Rhodamine B on Pils Shell (a) 10 and (b) 25°

particle and the values of partial molar free energy were 1695.58, 1303.26, 1303.26, 1176.96 & 1037.96 calories/mole respectively. At 25°C the amount adsorbed were 85.0, 85.0, 83.33, 81.25 & 79.0 percent and the partial molar free energy values were 1130.68, 1130.68, 1067.88, 997.68 & 930.14 calories/mole respectively (Table 6 & 6a). On increasing the dye concentrations the curves showed an increase in the amount of dye adsorbed at both the temperatures (Fig. 32).

Trypsan blue:

This dye was adsorbed to the extent of 85.0, 65.0, 58.33, 51.25 & 45.0 percent for its increasing order of initial concentrations at 10°C on 120 mesh particle size of Pila shells and the values of partial molar free energy were 1073.76, 594.19, 495.51, 406.65 & 338.37 calories/mole respectively. The Trypsan blue's adsorptions were 70.0, 57.5, 53.33, 47.5 & 42.0 percent for the same order of initial dye concentrations at 25°C. The corresponding values of partial molar free energy were 717.56, 509.97, 454.23, 384.03 & 324.65 calories/mole (Table 5 & 5a). The curves showed an increase in the amount of dye adsorbed on increase of concentrations at both the temperatures (Fig. 27).

Table - 6. Adsorption of dyes on Pila shells (Particle size: 80 Mesh)

Initial dye concentration ($1 \times 10^4 \mu\text{g/L}$)	Temperature 10°C		Temperature 25°C	
	Equilibrium dye concentration ($1 \times 10^4 \mu\text{g/L}$)	Amount of dye adsorbed ($\mu\text{g}/0.5\text{g}$)	Equilibrium dye concentration ($1 \times 10^4 \mu\text{g/L}$)	Amount of dye adsorbed ($\mu\text{g}/0.5\text{g}$)
Toluidine blue:				
200	40	160	70	130
400	140	260	200	200
600	250	350	300	300
800	380	420	430	370
1000	530	470	570	430
Crystal violet:				
200	10	190	30	170
400	40	360	60	340
600	60	540	100	500
800	100	700	150	650
1000	160	840	210	790
Trypsan blue:				
200	70	130	100	100
400	200	200	220	180
600	310	290	350	250
800	440	360	490	310
1000	600	400	640	360

Contd.....

Continuation of Table - 6.

Rhodamine B:

200		100		100		120		80
400		250		150		270		130
600		410		190		430		170
800		610		190		630		170
1000		810		190		830		170

Methylene blue:

200		10		190		30		170
400		60		340		90		310
600		110		490		160		440
800		200		600		280		520
1000		350		650		460		540

Methyl red:

200		00		200		20		180
400		40		360		60		340
600		90		510		100		500
800		150		650		190		610
1000		260		740		300		700

On 80 mesh particle size of adsorbent, 65.0, 50.0, 48.33, 45.0 & 40.0 percent adsorbate adsorbed at 10°C for increasing order of initial dye concentrations respectively and the respective values of partial molar free energy were 594.19, 392.32, 373.76, 338.37 & 289.12 calories/mole. The adsorptions at 25°C were 50.0, 45.0, 41.66, 38.75 & 36.0 percent and the partial molar free energy values were 413.11, 356.31, 321.24, 292.16 & 265.98 calories/mole respectively (Table 6 & 6a). The curves at 10°C and 25°C were of similar nature as above (Fig. 33).

Rhodamine B:

At temperature 10°C the adsorptions of Rhodamine B were 70.0, 47.5, 36.66, 26.65 & 23.0 percent for increasing initial dye concentrations on 120 mesh particle size of Pila shells and the respective values of partial molar free energy were 681.44, 364.7, 258.52, 172.32 & 147.93 calories/mole. For the same initial concentrations the adsorptions were 60.0, 42.5, 30.0, 23.75 & 19.0 percent at 25°C and the corresponding values of partial molar free energy were 546.1, 329.81, 212.57, 161.60 & 125.58 calories/mole (Table 5 & 5a). The curves at both the temperatures showed a little

Table 6 a. Adsorption of dyes on Pila Shells (Particle size :80 mesh)

Initial dye concentration (1×10^4 ug/L)	TEMPERATURE 10°C		TEMPERATURE 25° C	
	Percent adsorption	Partial molar free energy $-\bar{G}$ (Cals/Mole)	Percent adsorption	Partial molar free energy $-\bar{G}$ (Cals/Mole)

Toluidine blue:

200	80.0	910.94	65.00	625.69
400	65.0	594.19	50.00	413.11
600	58.33	495.51	50.00	413.11
800	52.50	421.35	46.25	370.01
1000	47.0	359.34	43.0	335.02

Crystal violet:

200	95.0	1695.58	85.00	1130.68
400	90.0	1303.26	85.0	1130.68
600	90.0	1303.26	83.33	1067.88
800	87.5	1176.96	81.25	997.68
1000	84.0	1037.96	79.0	930.14

Trypsan blue:

200	65.00	594.19	50.00	413.11
400	50.0	392.32	45.0	356.31
600	48.33	373.76	41.66	321.24
800	45.0	338.37	38.75	292.16
1000	40.0	289.12	36.0	265.98

Continuation of table 6 a:

Rhodamine B:

200		50.0		392.32		40.0		304.45
400		37.5		266.02		32.5		234.25
600		31.66		215.51		28.33		198.55
800		23.75		153.47		21.25		142.37
1000		19.0		119.26		17.0		111.05

Methylene blue:

200		95.0		1695.58		85.0		1130.68
400		85.0		1073.76		77.5		889.02
600		81.66		960.19		73.33		787.76
800		75.0		784.64		65.0		625.69
1000		65.0		594.19		54.0		462.81

Methyl red:

200		100.0		3001.68		90.0		1372.34
400		90.0		1303.26		85.0		1130.68
600		85.0		1073.76		83.33		1067.88
800		81.25		947.47		76.25		856.80
1000		74.0		762.44		70.0		717.56

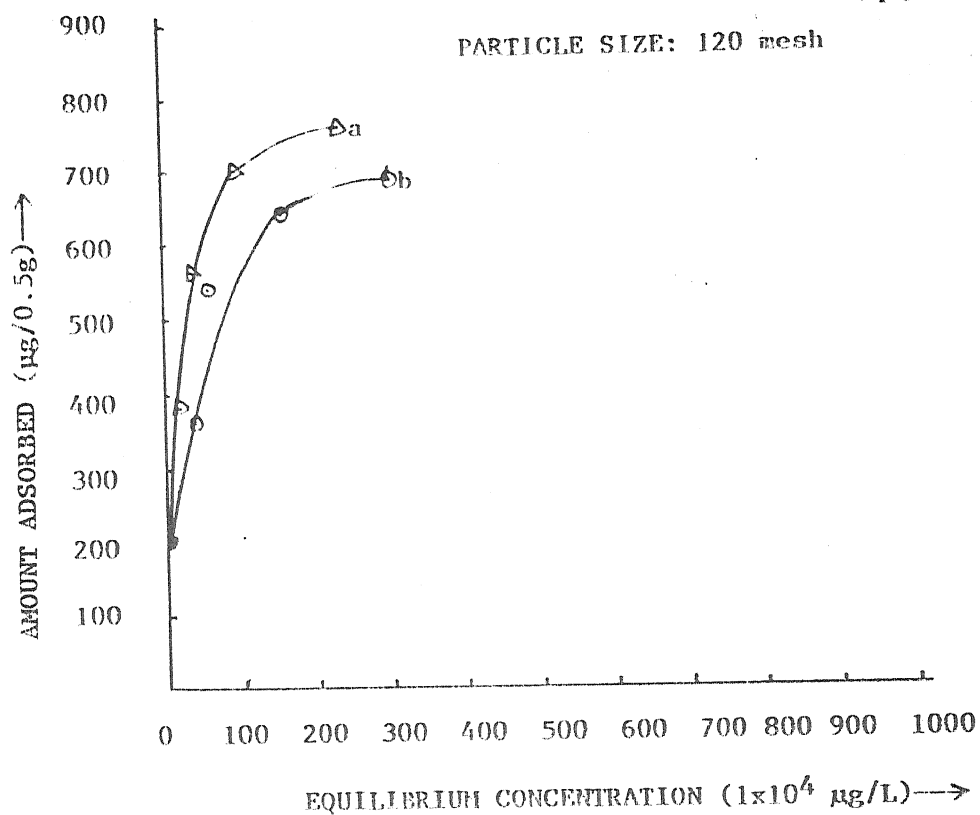


Fig.29: Adsorption Isotherms for Methylene blue on Pila Shell (a) 10 and (b) 25°

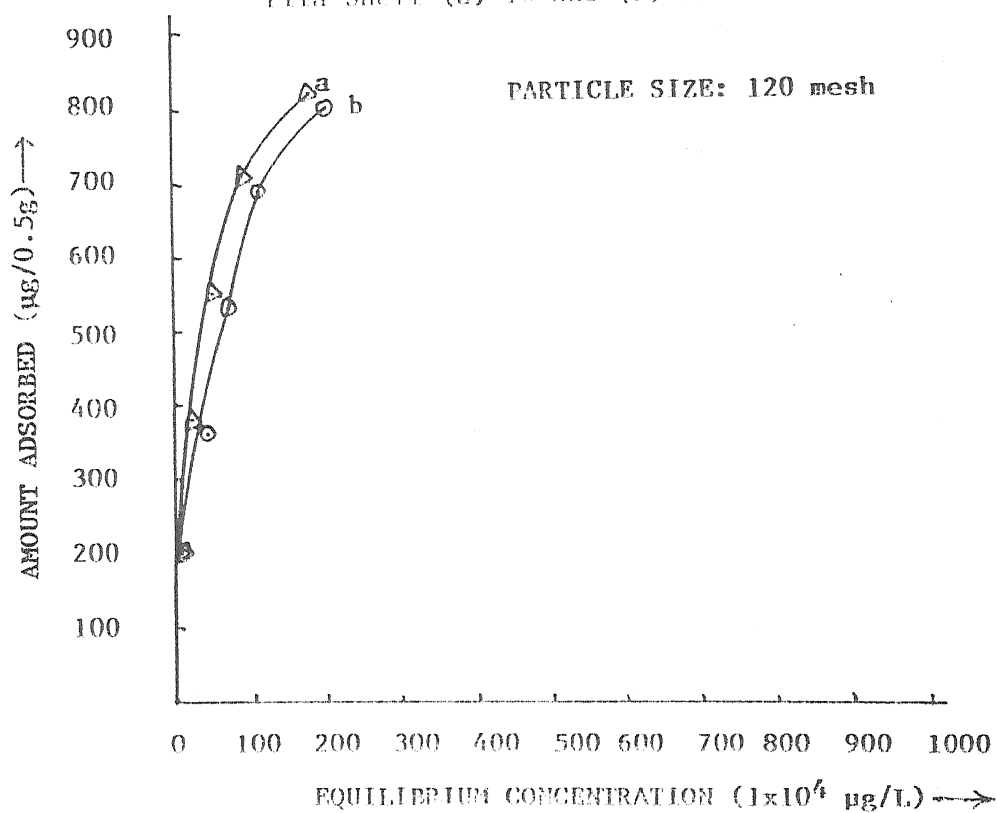


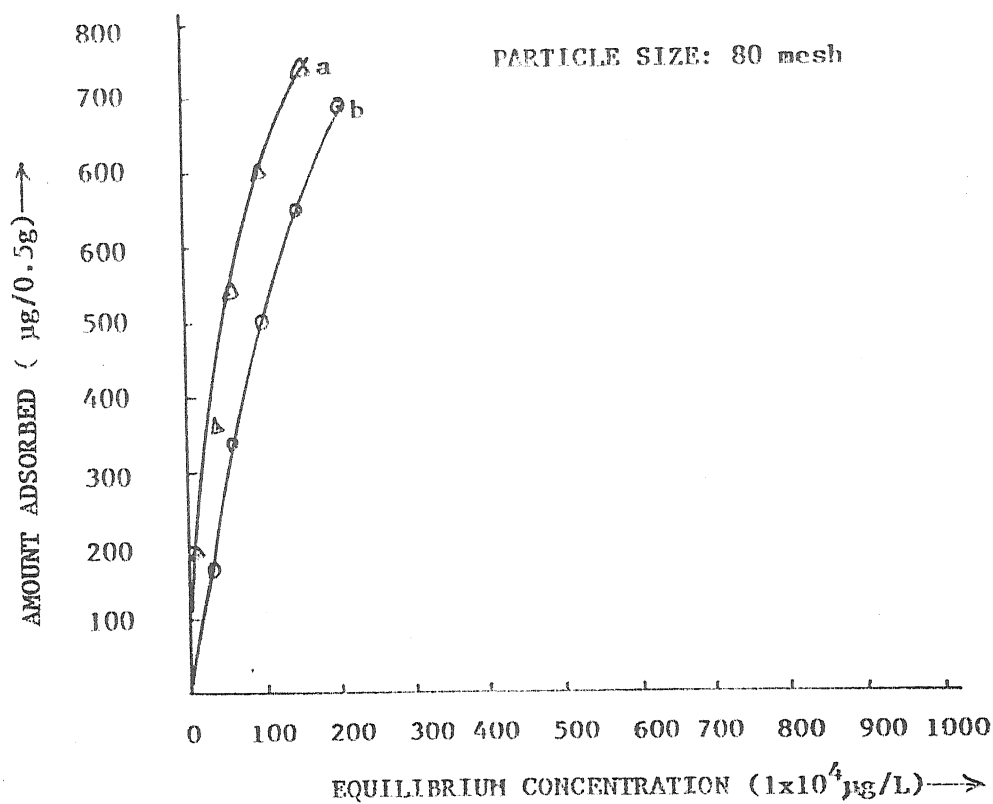
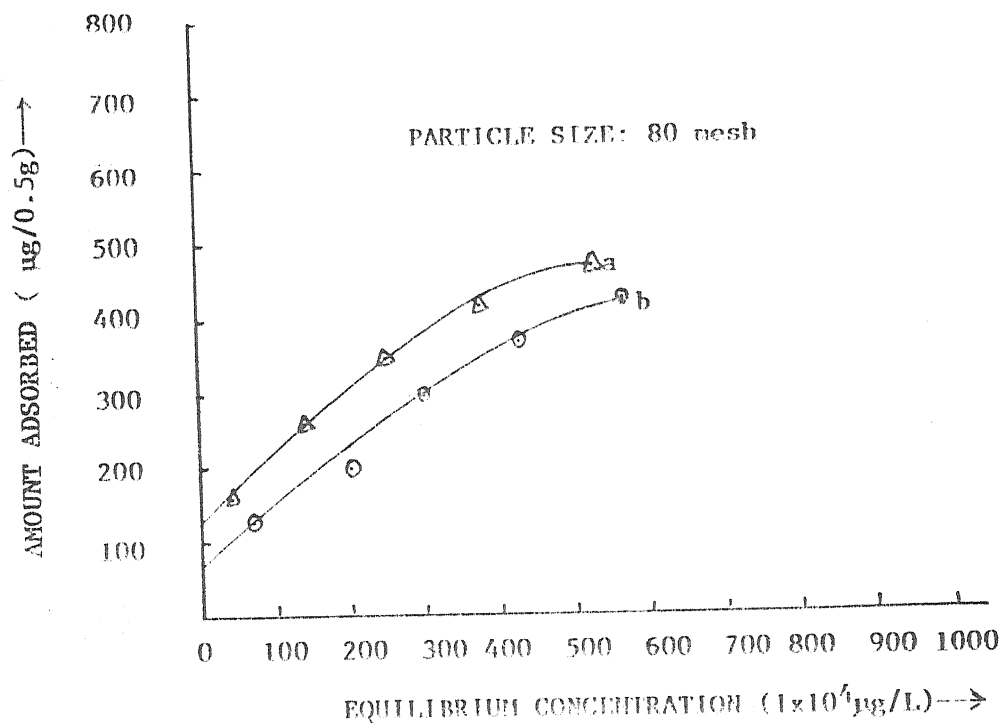
Fig.30: Adsorption Isotherms for Methyl red on Pila Shell (a) 10 and (b) 25°

increase in the amount of dye adsorbed on increasing order of concentrations (Fig. 28).

On 80 mesh particle size of Pila shells the adsorptions of Rhodamine B were 50.0, 37.5, 31.66, 23.75 & 19.0 percent respectively for increasing initial concentrations at 10°C and the respective partial molar free energy values were 392.32, 266.02, 215.51, 153.47 & 119.26 calories/mole. The adsorptions for the same concentrations were 40.0, 32.5, 28.33, 21.25 & 17.0 percent respectively at 25°C and their values of partial molar free energy were 304.45, 234.25, 198.55, 142.37 & 111.05 calories/mole (Table 6 & 6a). The nature of curves showed similarity with the above curves at both the temperatures (Fig. 34).

Methylene blue:

On increasing order of initial dye concentrations of Methylene blue the adsorptions were 100.0, 95.0, 93.33, 87.5 & 76.0 percent respectively on 120 mesh particle size of Pila shells at 10°C and the calculated values of partial molar free energy were 3001.68, 1695.58, 1532.75, 1176.96 & 807.74 calories/mole and at 25°C the adsorptions were 100.0, 90.0, 90.0, 80.0 & 69.0 percent for the same



order of initial concentrations and their corresponding values of partial molar free energy were 3160.78, 1372.34, 1372.34, 959.22 & 698.02 calories/mole (Table 5 & 5a). The curves at both the temperatures showed an steep increase in the amount of dye adsorbed at the beginning of the increase of initial dye concentrations and then a slow rise on increasing the further concentrations (Fig. 29).

On 80 mesh particle size of Pila shells, 95.0, 85.0, 81.66, 75.0 & 65.0 percent Methylene blue was adsorbed at 10°C for the aforesaid initial dye concentrations respectively and the respective values of partial molar free energy were 1695.58, 1073.76, 960.19, 784.64 & 594.19 calories/mole. At 25°C the adsorptions were 85.0, 77.5, 73.33, 65.0 & 54.0 percent and the corresponding partial molar free energy values were 1103.68, 889.02, 787.76, 625.69 & 462.81 calories/mole. The nature of curves at both the temperatures was same as above (Fig. 35).

Methyl red:

The adsorptions of Methyl red for its increasing initial concentrations were 100.0, 95.0, 91.66, 88.75 & 82.0 percent

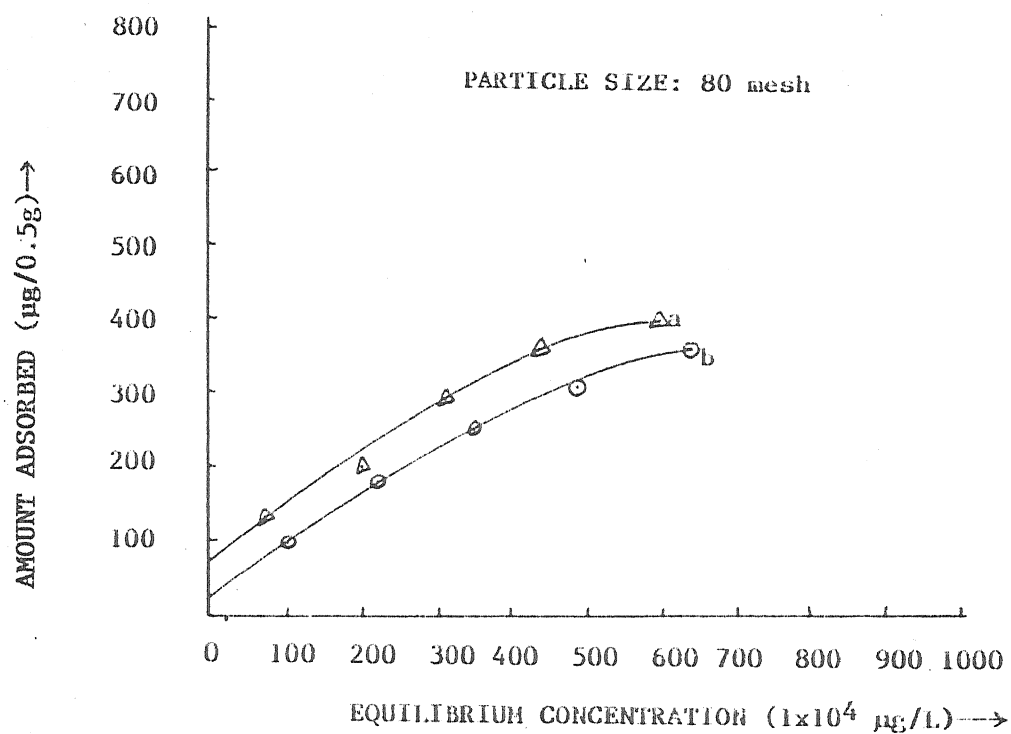


Fig. 33: Adsorption Isotherms for Trypan blue on P11a Shell (a) 10 and (b) 25°

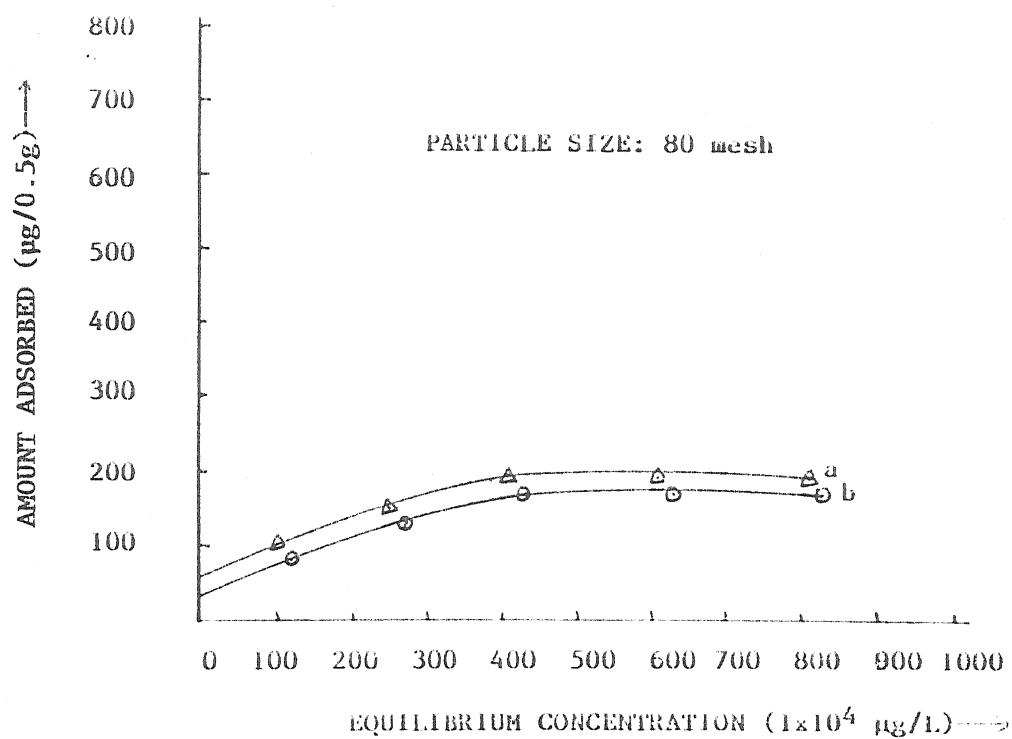


Fig. 34: Adsorption Isotherms for Rhodamine B on P11a Shell (a) 10 and (b) 25°

respectively on 120 mesh particle size of Pila shells at 10°C and the respective values of partial molar free energy were 3001.68, 1695.58, 1406.45, 1236.59 & 970.57 calories/mole. For the same order of initial concentrations the adsorptions were 100.0, 90.0, 88.33, 86.25 & 80.0 percent at 25°C and the partial molar free energy values were 3160.78, 1372.34, 1280.46, 1182.54 & 959.22 calories/mole respectively (Table 5 & 5a). The curves showed a high increase in the amount of dye adsorbed on increase of the concentrations (Fig. 30).

The adsorptions of the adsorbate were 100.0, 90.0, 85.0, 81.25 & 74.0 percent on 80 mesh particle size of the adsorbent at 10°C and the partial molar free energy values were 3001.68, 1303.26, 1073.76, 947.47 & 762.44 calories/mole respectively. At 25°C the amounts of adsorbate adsorbed were 90.0, 85.0, 83.33, 76.25 & 70.0 percent and the respective values of partial molar free energy were 1372.34, 1130.68, 1067.88, 856.80 & 717.56 calories/mole (Table 6 6a). The curves showed an increase in the amount adsorbed, on increase of concentrations (Fig. 36).

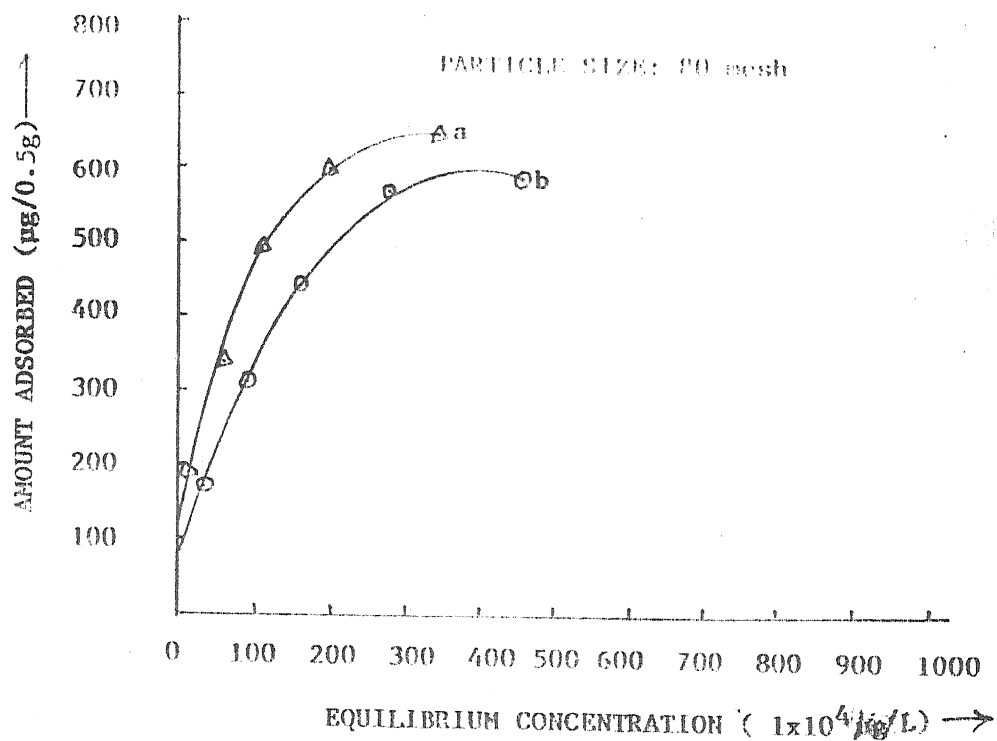


Fig. 35: Adsorption Isotherms for Methylene blue on Pila Shell (a) 10 and (b) 25°

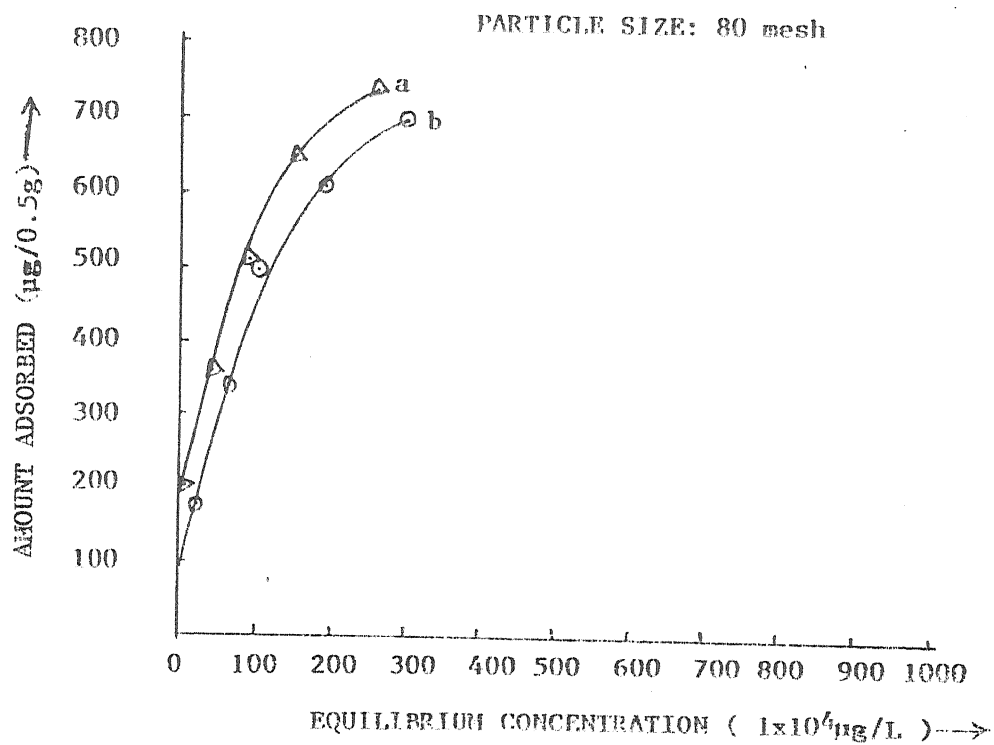


Fig. 36: Adsorption Isotherms for Methyl red on Pila Shell (a) 10 and (b) 25°

ADSORPTION OF DYES FROM EFFLUENTS ON PILA SHELLS

Red coloured effluent:

The adsorptions of dye from red coloured effluent were 100.0, 97.5, 91.66, 87.50 & 79.0^{percent} respectively for 20.0 40.0, 60.0 80.0 & 100.0 percent initially concentrated effluent solutions at 10°C on 120 mesh particle size of Pila shells. Values of partial molar free energy were 3001.68, 2087.90, 1406.45, 1176.96 & 883.32 calories/mole respectively. At 25°C, adsorptions were 100.0 95.0, 90.0, 82.5 & 76.0 percent for increasing order of initial concentrations and the values of partial molar free energy were 3160.78 1785.45, 1372.34, 1038.80 & 850.56 calories/mole respectively (Table 7 & 7a). The curves at both the temperatures indicated a gradual increase in the amount of dye adsorbed on increase of concentrations (Fig. 37).

On 80 mesh particle size (Temperature:10°C), adsorptions were 85.0, 85.0, 85.0, 80.0 & 73.0 percent for the aforesaid order of initial concentrations respectively and the respective values of partial molar free energy were 1073.76, 1073.76, 1073.76, 910.94 &

Table - 7. Adsorption of dyes from effluents on Pila Shells
(particle size: 120 Mesh)

Initial dye concentration (Percent)	Temperature 10°C		Temperature 25°C	
	Equilibrium	Amount of	Equilibrium	Amount of
	dye concent-	dye	dye concent-	dye
	ration	adsorbed	ration	adsorbed
	(Percent)	(Percent / 0.5g)	(Percent)	(Percent / 0.5g)

Red coloured effluent:

20	0	20	0	20
40	1	39	2	38
60	5	55	6	54
80	10	70	14	66
100	21	79	24	76

Violet coloured effluent:

20	2	18	4	16
40	10	30	13	27
60	21	39	24	36
80	32	48	35	45
100	50	50	54	46

Sky blue coloured effluent:

20	5	15	8	12
40	16	24	18	22
60	26	34	29	31
80	38	42	41	39
100	55	45	60	40

Contd.....

Continuation of Table - 7.

Yellow coloured effluent:

20		8		12		9		11
40		20		20		21		19
60		30		30		33		27
80		43		37		46		34
100		61		39		65		35

Green coloured effluent:

20		0		20		0		20
40		5		35		7		33
60		12		48		14		46
80		21		59		24		56
100		35		65		38		62

Orange coloured effluent:

20		0		20		2		18
40		5		35		7		33
60		12		48		14		46
80		21		59		25		55
100		32		68		36		64

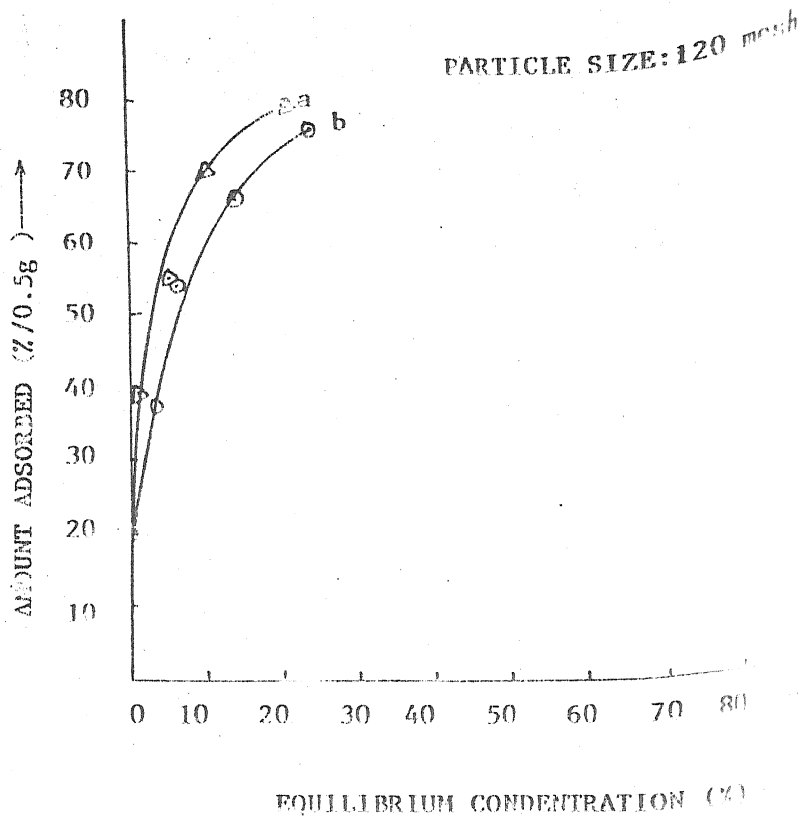


Fig:37: Adsorption isotherms for Red 60B effluent on Pila shell (a) 10% (b) 20%

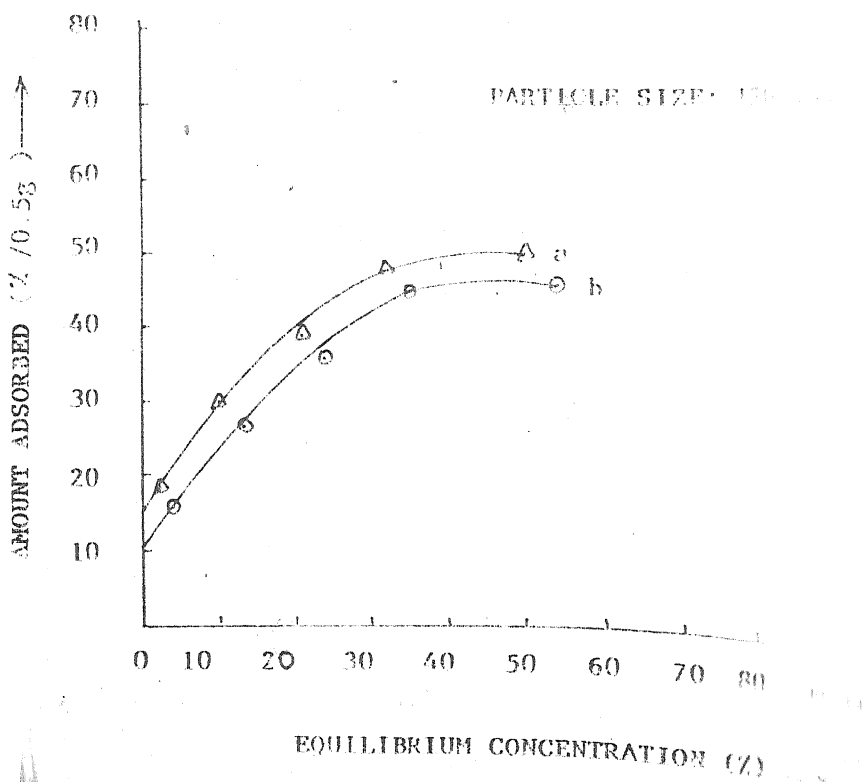


Fig:38: Adsorption isotherms for violet effluent on Pila shell (a) 10% (b) 20%

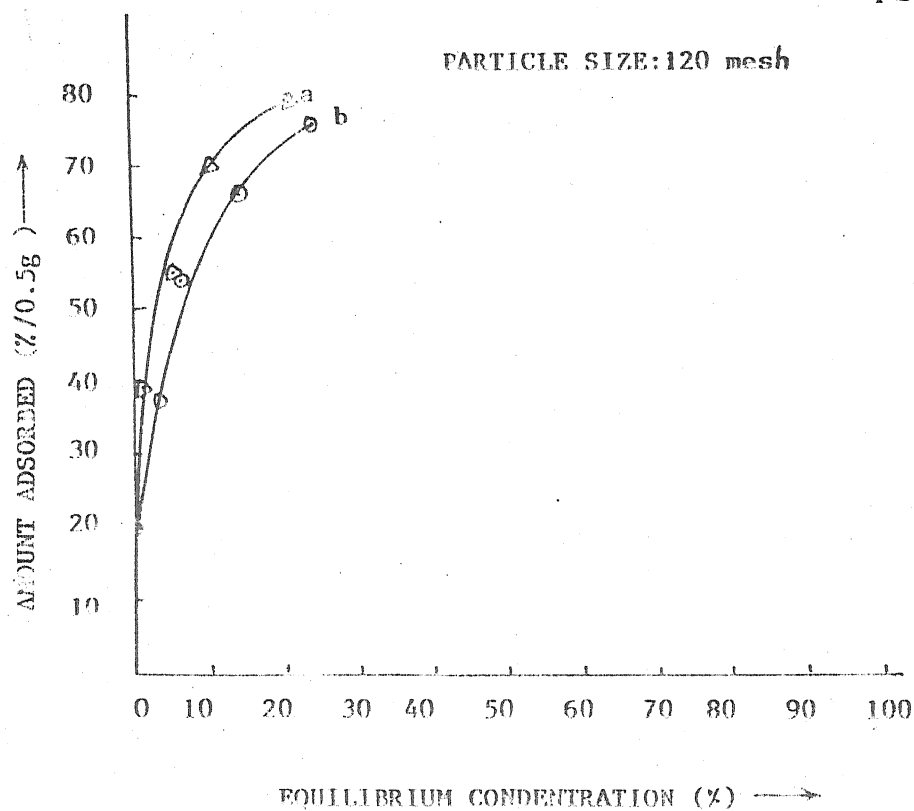


Fig:37: Adsorption isotherms for Red Coloured effluent on Pila shell (a) 10 & (b) 25°

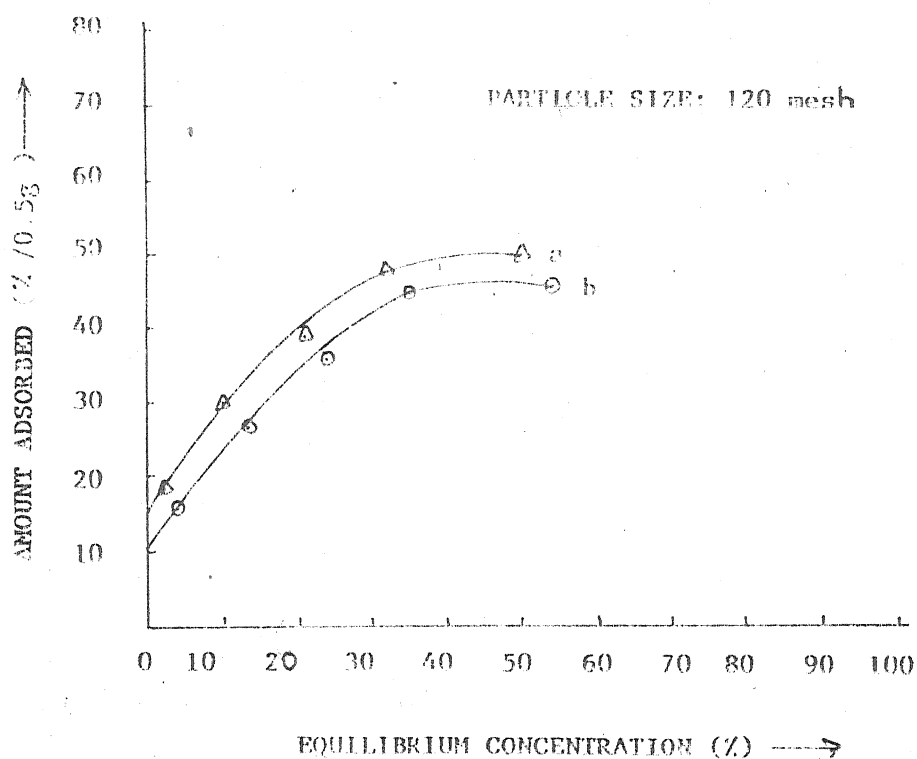


Fig:38: Adsorption isotherms for violet coloured effluent on Pila shell (a) 10 & (b) 25°

741.08 calories/mole. The percent adsorptions at 25°C were 80.0, 80.0, 80.0, 77.5 & 71.0 and their values of partial molar free energy were 959.22, 959.22, 959.22, 889.02 & 737.77 calories/mole respectively (Table 8 & 8a). The curves showed an increase in the amount of adsorbate adsorbed on increasing the concentrations at temperature 10 and 25°C (Fig. 43).

Violet coloured effluent:

At temperature 10°C, adsorptions of dye from violet coloured effluent were 90.0, 75.0, 65.0, 60.0 & 50.0 percent on Pila shells (particle size: 120 mesh) for 20.0, 40.0, 60.0, 80.0 & 100.0 percent initially dye concentrated effluent solutions respectively and the corresponding values of partial molar free energy were 1303.26, 784.64, 594.19, 518.62 & 392.32 calories/mole. The adsorptions were 80.0, 67.5, 60.0, 56.25 & 46.0 percent at 25°C and values of partial molar free energy were 959.22, 669.86, 546.10, 492.70 & 367.24 calories/mole (Table 7 & 7a). On increase of concentrations the curves showed an increase in the amount of dye adsorbed at temperature 10 and 25°C (Fig. 38).

Table 7 a: Adsorption of dyes from effluents on Pila Shells
(Particle size : 120 mesh)

Initial dye	TEMPERATURE 10°C		TEMPERATURE 25°C	
concentration	Percent	Partial molar	Percent	Partial molar
(Percent)	adsorption	free energy	adsorption	free energy
		$-\bar{G}(\text{Cals/Mole})$		$-\bar{G}(\text{Cals/Mole})$

Red coloured effluent:

20	100.0	3001.68	100.0	3160.78
40	97.5	2087.90	95.0	1785.45
60	91.66	1406.45	90.00	1372.34
80	87.50	1176.96	82.5	1038.80
100	79.0	883.32	76.0	850.56

Violet coloured effluent:

20	90.0	1303.26	80.0	959.22
40	75.0	784.64	67.5	669.86
60	65.0	594.19	60.0	546.10
80	60.0	518.62	56.25	492.70
100	50.0	392.32	46.0	367.24

Sky blue coloured effluent:

20	75.0	784.64	60.0	546.10
40	60.0	518.62	55.0	475.91
60	56.66	473.31	51.66	433.32
80	52.5	421.35	48.75	398.39
100	45.0	338.37	40.0	304.45

Continuation of table 7 a;

Yellow coloured effluent:

20		60.0		518.62		55.0		475.91
40		50.0		392.32		47.5		384.03
60		50.0		392.32		45.0		356.31
80		46.25		351.38		42.5		329.81
100		39.0		279.77		35.0		256.74

Green coloured effluent:

20		100.0		3001.68		100.0		3160.78
40		87.50		1176.96		82.5		1038.80
60		80.0		910.94		76.66		867.35
80		73.75		757.02		70.0		717.56
100		65.0		594.19		62.0		576.68

Orange coloured effluent:

20		100.0		3001.68		90.0		1372.34
40		87.50		1176.96		82.5		1038.80
60		80.0		910.94		76.66		867.35
80		73.75		757.02		68.75		693.23
100		68.0		644.91		64.0		608.90

At 10°C (particle size :80 mesh), 70.0, 67.5, 58.33, 55.0, & 46.0 percent adsorptions were observed for same order of above said initial concentrations respectively. The corresponding partial molar free energy values were 681.44, 636.14, 495.51, 451.95 & 348.76 calories/mole. At 25°C, the adsorptions were 60.0, 55.0, 55.0, 50.0, & 44.0 percent. The respective values of partial molar free energy were 546.10, 475.91, 475.91, 413.11 & 345.57 calories/mole (Table 8 & 8a). The curves at both the temperatures were almost similar in nature as above (Fig. 44).

Sky blue coloured effluent:

The experiments showed that on 120 mesh particle size of Pila shells the dye from sky blue coloured effluent adsorbed were 75.0, 60.0, 56.66, 52.5 & 45.0 percent respectively for increasing order of initially dye concentrated effluent viz. 20.0, 40.0, 60.0, & 80.0 & 100.0 percent at 10°C. The respective values of partial molar free energy were 784.64, —, 518.62, 473.31, 421.35 & 338.37 calories/mole. The amounts of adsorbate adsorbed on adsorbent at 25°C were 60.0, 55.0, 51.66, 48.75 & 40.0 percent for the effluent

Table - 8. Adsorption of dyes from effluents on Pila Shells
(Particle size: 80 Mesh)

Initial dye concentration (Percent)	Temperature 10°C		Temperature 25°C	
	Equilibrium	Amount of	Equilibrium	Amount of
	dye concent-	dye	dye concent-	dye
	ration	adsorbed	ration	adsorbed
	(Percent)	(Percent/0.5g)	(Percent)	(Percent/0.5g)

Red coloured effluent:

20	3	17	4	16
40	6	34	8	32
60	9	51	12	48
80	16	64	18	62
100	27	73	29	71

Violet coloured effluent:

20	6	14	8	12
40	13	27	18	22
60	25	35	27	33
80	36	44	40	40
100	54	46	56	44

Sky blue coloured effluent:

20	8	12	9	11
40	18	22	20	20
60	29	31	31	29
80	41	39	45	35
100	58	42	61	39

Contd.....

Continuation of Table - 8.

Yellow coloured effluent:

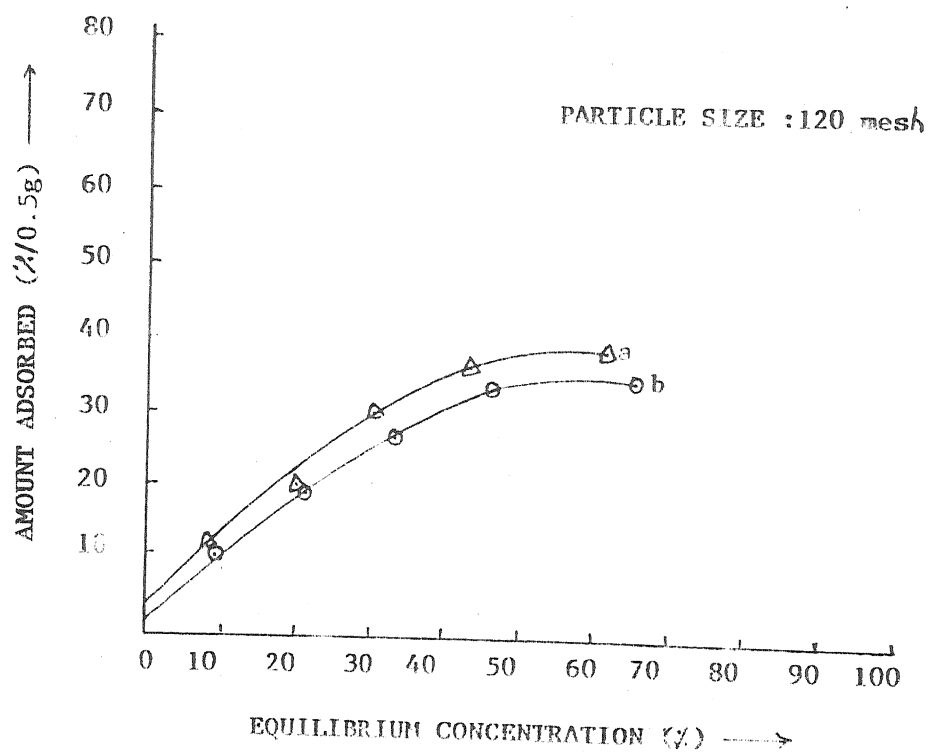
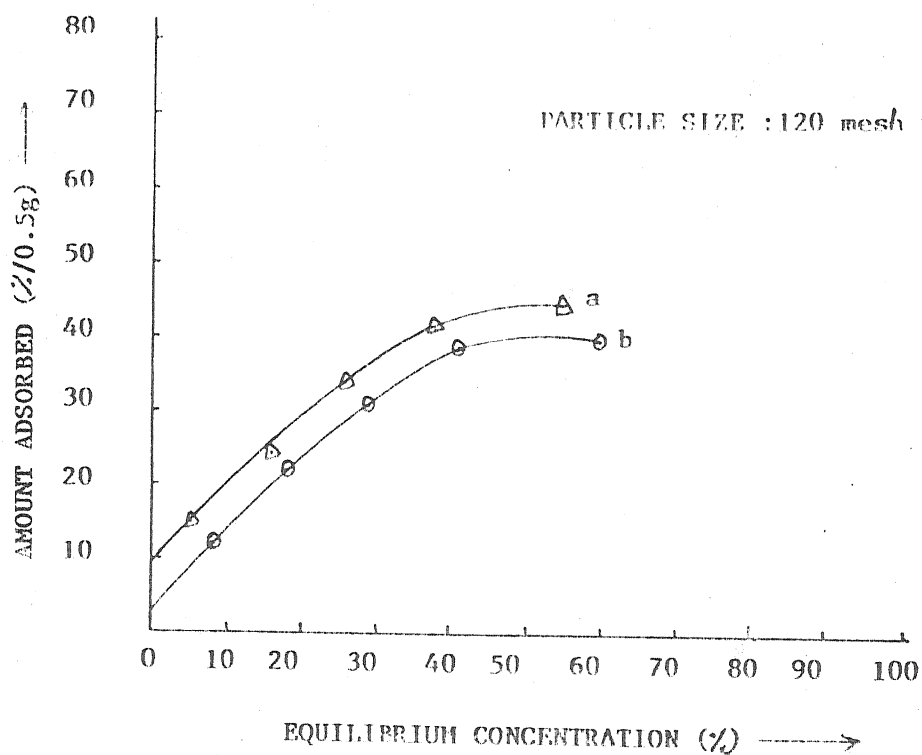
20		9		11		11		9
40		23		17		24		16
60		34		26		36		24
80		48		32		51		29
100		64		36		68		32

Green coloured effluent:

20		3		17		5		15
40		8		32		11		29
60		16		44		18		42
80		26		54		29		51
100		38		62		41		59

Orange coloured effluent:

20		1		19		3		17
40		7		33		9		31
60		16		44		18		42
80		24		56		27		53
100		37		63		40		60



concentrated similarly as above and the values of partial molar free energy were 546.10, 475.91, 433.32, 398.39 & 304.45 calories/mole (Table 7 & 7a). The curves at both the temperatures showed that the higher the concentration the greater was the amount of dye adsorbed (Fig. 39).

On increasing order of initial dye concentrations in the effluent the adsorptions were 60.0, 55.0, 51.66, 48.75 & 42.0 percent on 80 mesh particle size of Pila shells at 10°C. The respective values of partial molar free energy were 518.62, 451.95, 411.50, 378.34 & 308.31 calories/mole. The adsorptions at 25°C were 55.0, 50.0, 48.33, 43.75 & 39.0 percent. For which the partial molar free energy values were 475.91, 413.11, 393.57, 342.91 & 294.60 calories/mole respectively (Table 8 & 8a). There were the similarities with the above in the nature of curves at both the temperatures (Fig. 45).

Yellow coloured effluent:

60.0, 50.0, 50.0, 46.25 & 39.0 percent adsorbate were adsorbed respectively for 20.0, 40.0, 60.0, 80.0 & 100.0 percent dye

Table 8 a: Adsorption of dyes from effluents on Pila Shells

(Particle size :80 mesh)

Initial dye	TEMPERATURE 10°C		TEMPERATURE 25°C	
concentration	Percent	Partial molar	Percent	Partial molar
(Percent)	adsorption	free energy	adsorption	free energy
		$-\bar{G}(\text{Cals/Mole})$		$-\bar{G}(\text{Cals./Mole})$

Red coloured effluent:

20	85.0	1073.76	80.0	959.22
40	85.0	1073.76	80.0	959.22
60	85.0	1073.76	80.0	959.22
80	80.0	910.94	77.5	889.02
100	73.0	741.08	71.0	737.77

Violet coloured effluent:

20	70.0	681.44	60.0	546.10
40	67.5	636.14	55.0	475.91
60	58.33	495.51	55.0	475.91
80	55.0	451.95	50.0	413.11
100	46.0	348.76	44.0	345.57

Sky blue coloured effluent:

20	60.0	518.62	55.0	475.91
40	55.0	451.95	50.0	413.11
60	51.66	411.50	48.33	393.57
80	48.75	378.34	43.75	342.91
100	42.0	308.31	39.0	294.60

Continuation of table 8 a:

Yellow coloured effluent:

20		55.0		451.95		45.0		356.31
40		42.5		313.21		40.0		304.45
60		43.33		321.47		40.0		304.45
80		40.0		289.12		36.25		268.31
100		36.0		252.59		32.0		229.85

Green coloured effluent:

20		85.0		1073.76		75.0		826.23
40		80.0		910.94		72.5		769.42
60		73.33		748.11		70.0		717.56
80		67.5		636.14		63.75		604.77
100		62.0		547.65		59.0		531.39

Orange coloured effluent:

20		95.0		1695.58		85.0		1130.68
40		82.5		986.52		77.5		889.02
60		73.33		748.11		70.0		717.56
80		70.0		681.44		66.25		647.36
100		63.0		562.74		60.0		546.10

concentrated yellow coloured effluent at 10°C on 120 mesh particle size of Pila shells and the respective values of partial molar free energy were 518.62, 392.32, 392.32, 351.38 & 279.77 calories/mole. At 25°C the adsorptions were 55.0, 47.5, 45.0, 42.5 & 35.0 percent and the partial molar free energy values were 475.91, 384.03, 356.31, 329.81 & 256.74 calories/mole respectively (Table 7 & 7a). The curves showed that the higher the values of concentrations the greater was the amount of dye adsorbed at both the temperatures (Fig.40).

On 80 mesh particle size of Pila shells (Temperature: 10°C) the adsorptions were 55.0, 42.5, 43.33, 40.0 & 36.0 percent respectively for the same order of initial dye concentrations, as above and the values obtained for partial molar free energy were 451.95, 313.21, 321.47, 289.12 & 252.59 calories/mole. At temperature 25°C the adsorptions were 45.0, 40.0, 40.0, 36.25 & 32.0 percent and the corresponding values of partial molar free energy were 356.31, 304.45, 304.45, 268.31 & 229.85 calories/mole (Table 8 & 8a). The curves showed a similarity in nature as above at both the temperatures (Fig. 46).

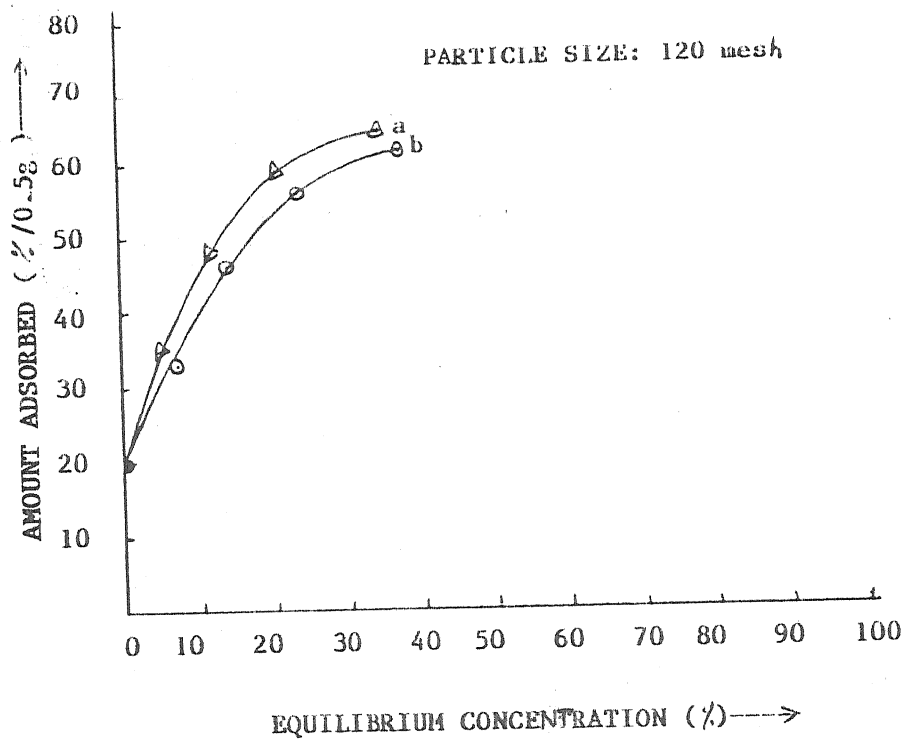


Fig.41: Adsorption isotherms for Green coloured effluent on Pila shell (a) 10 & (b) 25°

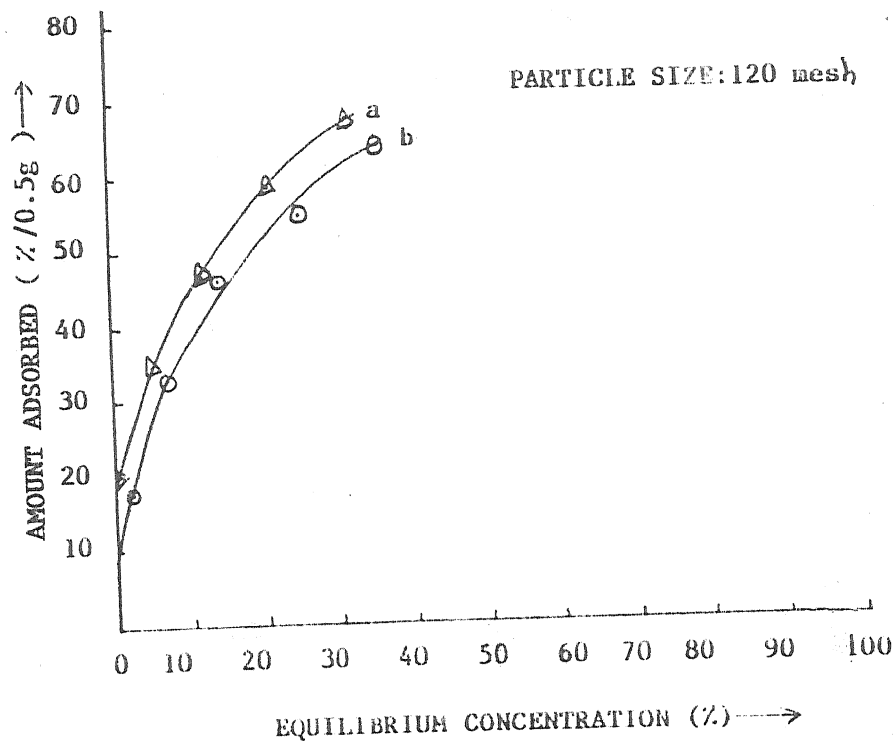


Fig.42: Adsorption isotherms for Orange coloured effluent on Pila shell (a) 10 and (b) 25°

Green coloured effluent:

At temperature 10°C the adsorptions of dye from green coloured effluent were 100.0, 87.50, 80.00, 73.75 & 65.00 percent respectively on Pila shells (particle size: 120 mesh) for 20.0, 40.0, 60.0, 80.0 & 100.0 percent initially dye concentrated adsorbate solutions and the corresponding values of partial molar free energy were 3001.68, 1176.96, 910.94, 757.02 & 594.19 calories/mole. For the same order of initially dye concentrated effluent the adsorptions were 100.0, 82.5, 76.66, 70.0 & 62.0 percent at 25°C with their partial molar free energy values of ~~3160.78~~, 1038.80, 867.35, ~~717.56~~ & ~~574.68~~ calories/mole respectively (Table 7 & 7a). At both the temperatures the curves showed an increase in the amount of dye adsorbed on increase of dye concentrations (Fig. 41).

The initial concentrations being unchanged the adsorptions on Pila shells (particle size: 80 mesh) were 85.0, 80.0, 73.33, 67.5 & 62.0 percent and the partial molar free energy values were 1073.76, 910.94, 748.11, 636.14 & 547.65 calories/mole respectively at 10°C . At 25°C the adsorptions in terms of percentage were 75.0, 72.5, 70.0, 63.75 & 59.0 (Table 8 & 8a) and the respective partial molar free

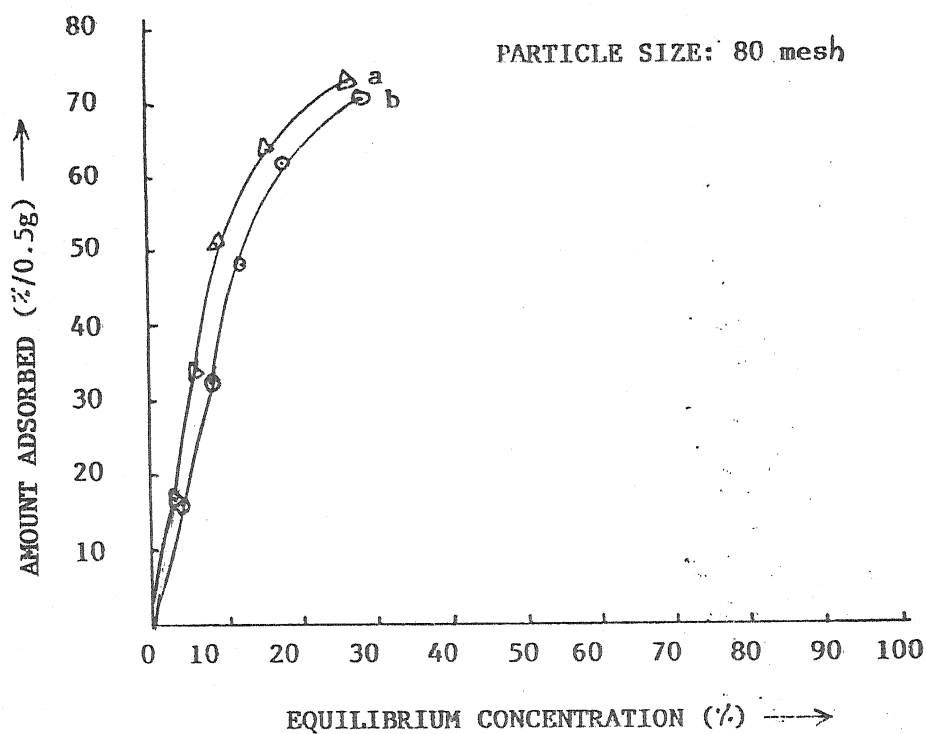


Fig:43: Adsorption isotherms for Red coloured effluent on Pila shell (a) 10 & (b) 25°

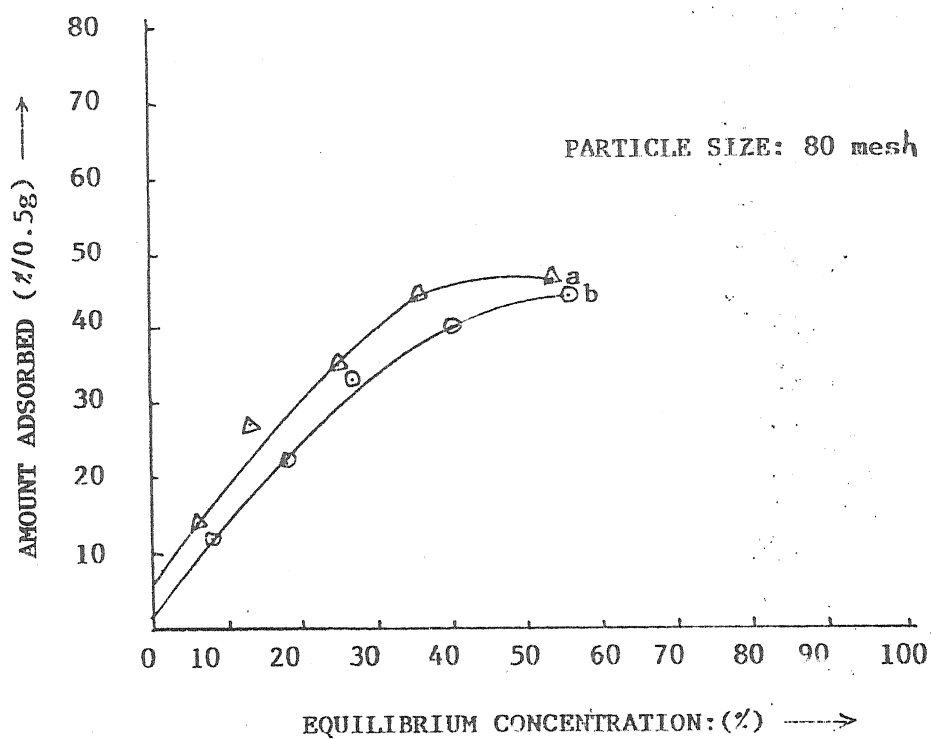


Fig:44: Adsorption isotherms for Violet coloured effluent on Pila shell (a) 10 & (b) 25°

energy values were 1130.68, 889.02, 717.56, 647.36 & 546.10 calories/mole. The curves were of similar nature as above at both the temperatures (Fig. 47).

Orange coloured effluent:

The results showed that on 120 mesh particle size of Pila shells, the adsorptions were 100.0, 87.5, 80.0, 73.75 & 68.0 percent at 10°C for 20.0, 40.0, 60.0, 80.0 & 100.0 percent dye concentrated orange coloured effluent respectively. The partial molar free energy values were 3001.68, 1176.96, 910.94, 757.02 & 644.91 calories/mole. At 25°C the adsorptions were 90.0, 82.5, 76.66, 68.75 & 64.0 respectively for the aforesaid increasing order of initial dye concentrations and the respective values of partial molar free energy were 1372.34, 1038.80, 867.35, 693.23 & 608.90 calories/mole (Table 7 & 7a). On increasing the dye concentrations the curves showed an increase in the amount of dye adsorbed at both the temperatures (Fig. 42).

For the same order of initially dye concentrated effluent as above, the adsorptions were 95.0, 82.5, 73.33, 70.0 & 63.0 percent respectively on 80 mesh particle size of Pila shells

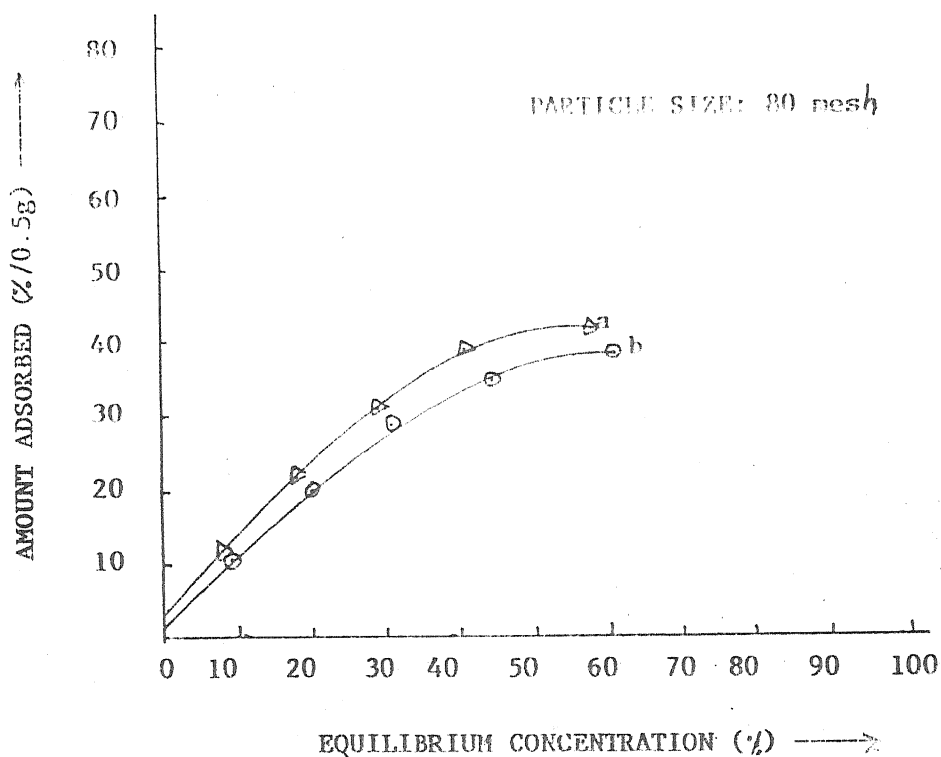


Fig:45: Adsorption isotherms for Sky blue coloured effluent on Pila shell (a) 10 & (b) 25°

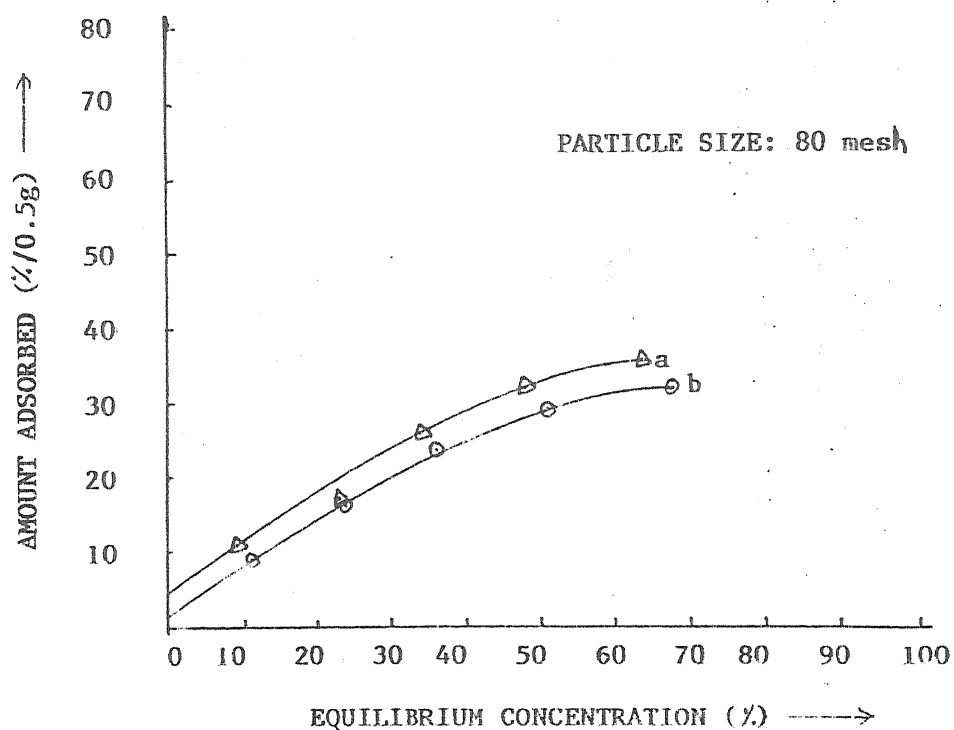


Fig:46: Adsorption isotherms for Yellow coloured effluent on Pila shell (a) 10 & (b) 25°

(Temperature 10°C) and the respective values obtained for partial molar free energy were 1695.58, 986.52, 748.11, 681.44 & 562.74 calories/mole. At 25°C the amounts of dye adsorbed were 85.0, 77.5, 70.0, 66.25 & 60.0 percent and the corresponding values of partial molar free energy were 1130.68, 889.02, 717.56, 647.36 & 546.10 calories/mole (Table 8 & 8a). In the nature of curves a similarity was observed with the above curves (Fig. 48).

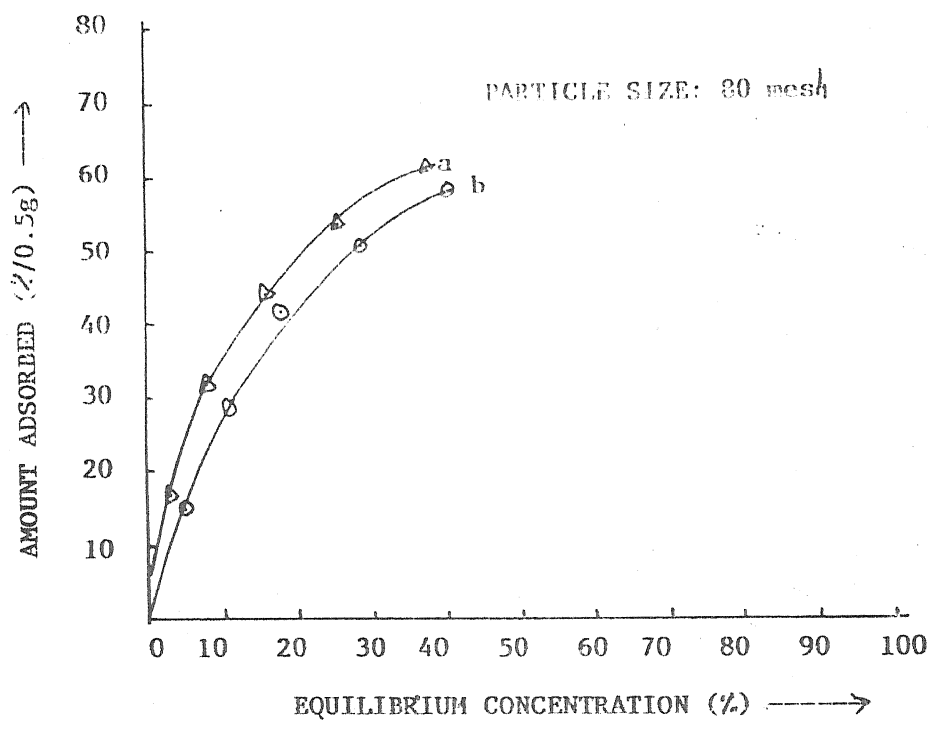


Fig:47: Adsorption Isotherms for Green coloured effluent on Pila shell (a) 10 & (b) 25°

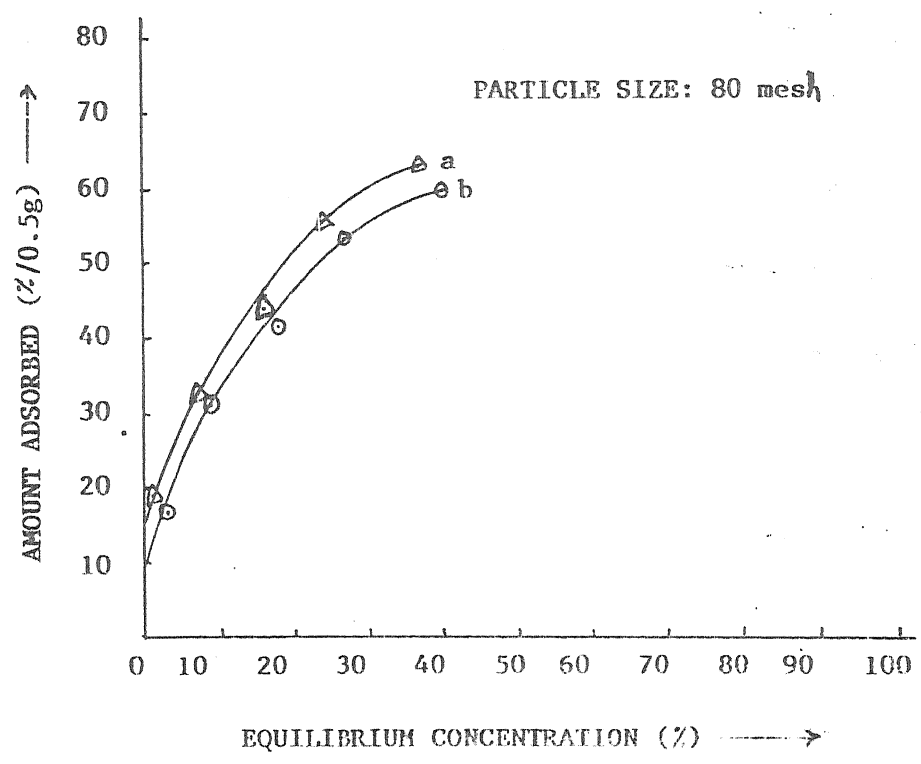


Fig:48: Adsorption isotherms for Orange coloured effluent on Pila shell (a) 10 & (b) 25°

D I S C U S S I O N

DISCUSSION

Highly significant adsorptions by the shells of Pila & Unio both, indicated their good adsorptive capacities. Adsorptions of some dyes up to the extent of 90.0 to 100.0 percent, although at high dilutions, put these shells in the category of good adsorbents. On comparative studies of the ongoing tables and isotherms, whether it was the adsorption of dyes from the prepared solutions OR from the effluents, irrespective of temperature (10°C or 25°C), particle size (80 mesh or 120 mesh) & concentrations, it was observed that the adsorptive capacity of Pila shell was higher than that of Unio shell.

All the dyes from prepared solutions and effluents exhibited adsorptions of high order on Pila shell. Some of them namely ; Crystal violet, Methylene blue & Methyl red were adsorbed 100.0 percent, whereas on Unio shell, only Methyl red was adsorbed cent percent (Table 1a & 5a). The 100.0 percent adsorptions were shown by the dyes from Red and Green coloured effluents (Table 3a & 7a). Among the dyes, this tendency was most prominently displayed by Toluidine blue on particle size 120 mesh. In the increasing order of the concentrations of prepared dye solutions, the adsorptions of this dye

on Pila shell at 10°C were 25.0, 12.50, 13.33, 13.75 & 11.0 percent more than that of Unio shell and this pattern was confirmed at 25°C, where the difference in adsorptions were 20.0, 7.50, 17.33, 12.5 & 10.0 percent. The adsorption figures at two different temperatures were in conformity with the behaviour of temperature towards adsorption [214,215]. The extent of adsorptions were also indicated by the values of partial molar free energy which increased with dilution and had high values for 100.0 percent adsorptions.

Though the shell of Pila indicated better adsorptive capacity than that of Unio, so far as their adsorptive behaviour is concerned towards dyes and effluents, the shells of both the animals showed similar nature of adsorption. That is Crystal violet, Methyl red & Methylene blue were adsorbed better than other dyes by both the shells, although to different extents in these two cases. Similarly, adsorptions from Red, Orange & Green effluents were higher on the two shells than from other effluents. The adsorptions of the six dyes on Pila shell were in the following decreasing order:-

Crystal violet > Methyl red > Methylene blue > Toluidine blue > Trypsan blue > Rhodamine B.

The dyes adsorbed on Unio shell were in the following order:-

Methyl red > Crystal violet > Methylene blue > Toluidine blue > Trypsan blue > Rhodamine B.

But the adsorptions from the effluents on both the shells were in the same order which was as under:-

Red > Orange > Green > Violet > Sky blue > Yellow.

The different order of adsorptions of dyes on Pila & Unio shells might be due to specific nature of adsorbates rather than of adsorbents, as both of which have same major chemical constituents.

In all the cases, it was observed that there were comparatively higher adsorptions at 10°C and lower at 25°C. This tendency confirmed the earlier findings [169,216,217]. Different views were forwarded for decrease of adsorptions with rise in temperature. Singh *et. al.* [100,182] suggested a decrease in adsorption with the rise of temperature, due to the exothermic nature of adsorption process, whereas Gunther *et. al.* [218] and Garrett [219] provided explanation for decrease of adsorption with rising temperature, owing to increase in solubility of adsorbate. In this connection one more explanation has been placed [25], according

to which desorption process started at higher temperatures. On the other hand contradictory findings were noticed wherein adsorption was found to increase with rise of temperature [169,186]. In view of the above contradictory findings regarding the effectiveness of temperature on adsorption, it might be possible to observe some cases where the temperature may not affect the adsorption, appreciably.

The finer particles of Pila & Unio (120 mesh) exhibited more adsorptions than 80 mesh particles. The effect of particle size was made visible by all the adsorbates. Some adsorbates showed 20 percent more adsorption which clearly indicated significant role of particle size. Finer the particles, more surface area of the adsorbents would be available. The increase in surface area of the adsorbents played a vital role in boosting the retainment of higher number of adsorbate particles, which was in conformity with the earlier investigation [182]. However insignificant increase in adsorption was reported by Dave [20]. Besides surface area, pore volumes were also found responsible for adsorptive character of the adsorbents [7,10,11].

Mirza et. al. observed that there was no direct relationship between the extent of adsorption and surface area. Surface area was

by no means the only physical property which could determine the extent of adsorption. Particularly for non-metallic solids, the pore structure was also a significant factor, which contributed the total surface area. Due to heterogeneity of the surfaces, the adsorption was not always directly proportional to the surface area [169].

It was observed without any exception that there was a systematic increase in adsorption in terms of percentage with increasing the dilution. It was highly noticeable in case of Methyl red and Red coloured effluent which were cent percent adsorbed at high dilutions. However the isotherms of Rhodamine B, after slow rise initially, got almost saturation, thus, showed insignificant rise in adsorptions. Any way increase in percent adsorption followed dilution. As far as the amounts of dyes adsorbed are concerned, there was a gradual increase in the net amounts of adsorbates on increase of their concentrations, on both the adsorbents viz. *Unio* & *Pila* shells. These investigations confirmed the earlier investigation [169].

In view of the above, the shells of *Unio* & *Pila* emerged to be good adsorbents, both in laboratory and industry as well. The

advantage of these shells as adsorbents lies in the fact that the shells are easily available in nature and without any chemical or other complicated process (except washing, grinding & activation), are readily available for adsorption. In the present age of industries and water crisis, these shells are convenient tools for adsorptions with the help of which purification of effluents can be performed to make reuse of water, leading to industrial processes economical; and maximum use of the same water through recycling.

Large scope is left for further studies on the adsorption aspects of these shells, wherein they can be employed to test their behaviours on other coloured, non-coloured and other impurities of water & non-aqueous liquids. It may not be strange if they could be good adsorbents for all the three states of matter i.e. solid, liquid and gas.

Conclusion:-

The aforesaid studies established the following:-

1. The shells of *Unio* & *Pila* were introduced as new adsorbents. They were cheap, easily available and good adsorbents.

2. Comparatively Pila shell emerged as better adsorbent than Unio shell.
3. Percentage adsorptions \propto dilution; and
net amount adsorbed \propto concentration.
4. The extent of adsorption depended upon
the particle size of the adsorbent.
5. The colour of adsorbent did not seem to
play any role in adsorption.
6. Adsorption $\propto \frac{1}{\text{Temperature}}$
7. Sufficient scope for further studies for these
adsorbents with a variety of other adsorbates
& different parameters.

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A P P E N D I C E S

TABLE 1

Adsorption of Iodine in Aqueous Medium

S. No.	Concentration of Iodine Solution	Moles of Iodine adsorbed/2g of powder		
		CaCO ₃	Pila Shell	Unio Shell
1	0.02 M	9.5×10^{-5}	12.5×10^{-5}	15.0×10^{-5}
2	0.015 M	10.5×10^{-5}	13.9×10^{-5}	16.5×10^{-5}
3	0.01 M	10.0×10^{-5}	13.0×10^{-5}	16.0×10^{-5}

TABLE 2

Adsorption of Iodine in Alcoholic Solution

S. No.	Concentration of Iodine Solution	Moles of Iodine adsorbed/2g of powder		
		CaCO ₃	Pila Shell	Unio Shell
1	0.02 M	18.0×10^{-5}	17.5×10^{-5}	16.0×10^{-5}
2	0.015 M	16.1×10^{-5}	15.0×10^{-5}	14.3×10^{-5}
3	0.01 M	12.8×10^{-5}	11.5×10^{-5}	11.5×10^{-5}

There was significant adsorption of iodine in all cases (Tables 1 & 2). The adsorptive capacities of the shell powders were higher than that of the calcium carbonate in aqueous solutions but slightly lower in alcoholic solutions; it might be attributed to the presence, though minute, of the organic matter in the shells (1 & 2), which as insoluble in aqueous medium might have contributed towards adsorption but has been ineffective in alcohol due to its dissolution.

Thus the shells of pila and unio have emerged to be good adsorbents, however, further studies would be needed to assess their overall suitability.

LETTER TO THE EDITOR

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